VOL. XIII. 1908

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OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

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VOLUME XIII.

THIRTEENTH GENERAL MEETING

ALBANY, N. Y., APRIL 30, MAY 1, 2, 1908.

PUBLISHED BY
THE AMERICAN ELECTROCHEMICAL SOCIETY
LEHIGH UNIVERSITY, SOUTH BETHLEHEM, PA.
1908

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April 30-May 2, 1908

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TABLE OF CONTENTS.

PAGE.

Proceedings of Thirteenth General Meeting..... 1
Report of Board of Directors..... 9
Report of the Secretary..... 10
Report of the Treasurer..... 13
Members Elected and Qualified..... 14

PRESIDENTIAL ADDRESS.

The Corrosion of Iron from the Electrochemical Standpoint—C. F. Burgess 17

PAPERS.

Electrochemical Corrosion of the Rochester Steel Conduit—Richard H. Gaines 55
Electrolytic Refining of Iron—Edward F. Kern.....103
Electrical Testing of Iron During the Annealing—E. E. F. Creighton..127
Electric Furnace Conversion of Iron Pyrites into a Magnetic Form—O. L. Kowalke.....133
The Alloying of Calcium and Iron—Alcan Hirsch and James Aston...143
The Preparation of Calcium Alloys for Aluminothermic Work—O. P. Watts and J. M. Breckenridge.....153
Industrial Application of Aluminum—E. Blough.....165
The Nature of the Surface Film Formed on Aluminum, and the Aluminum-Magnesium Cell—H. T. Barnes and G. W. Shearer.....169
The Use of Dry Cells on Ignition Service—J. W. Brown.....173
The Temperature Formula for the Weston Standard Cell—F. A. Wolff.187
The Principles Involved in the Selection and Definition of the Fundamental Units for International Adoption—F. A. Wolff.....213
The Construction and Accurate Measurement of Resistances of the Order of One Hundred Thousand Megohms—Howard L. Bronson 231
The Electrochemistry of Light—Wilder D. Bancroft.....243
On the Nature of Electrolytic Conductors—Louis Kahlenberg.....265
Direct Currents in Electrolytes without Electrodes—Carl Hering.....273
Reversed Electrolysis—J. W. Turrentine.....289
Electrolysis of Nitric Acid Using a Mercury Cathode—J. A. Wilkinson.309
Copper Anodes in Chloride Solutions—Saul Dushman.....313
The Solubilities of Boric, Camphoric, Benzoic and Salicylic Acids in Aqueous Ethyl Alcohol Solutions at 25°—Atherton Seidell.....319

Additional Experiments on the Electrolytic Corrosion of Brasses—A. T. Lincoln and G. C. Bartells, Jr. 331
The Early Work of Joseph Henry—James F. McElroy 339
Robert Hare's Electric Furnace—Charles A. Doremus 347
On the Direct Synthesis of Hydrocyanic Acid—E. W. Smith and R. S. Hutton 359
Distillation of Turpentine by Electricity—F. T. Snyder 371
Power for Electrochemical Industries—John Meyer 377
Forestry, Water Storage, Power and Navigation—Edward R. Taylor . 385
Kinetic Molecular Energy—Charles P. Steinmetz 397
The Absorption of the Radio-Active Emanations by Charcoal—R. W. Boyle 429
Electrochemical Patents, and Some Needs of the United States Patent System—Arba B. Marvin, Jr 431
The Latent Heat of Vaporization of Metals and Other Substances—Joseph W. Richards 447
Bibliography of Electrochemistry and Allied Subjects—P. F. Mottelay . 453
Memoir on the Methods of Treatment of Simple and Complex Ores of Molybdenum, Tungsten, Uranium, Vanadium: Part II, Tungsten. Gustave Gin 481
Advertisements . . . . . .

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VOLUME XIII. 1908.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE THIRTEENTH GENERAL MEETING OF THE SOCIETY, HELD AT ALBANY, N. Y., APRIL 30-MAY 2, 1908.

(Number of members registered, 75; guests, 60; total 135.)

SESSION OF APRIL 30th.

The morning meeting was called to order at 10.30 o'clock, in the ball room of the Hotel Ten Eyck, Albany, President C. F. Burgess in the chair.

Papers by H. L. Bronson, of McGill University; Dr. R. W. Boyle, of McGill University; Dr. E. F. Wolff, of the Bureau of Standards; J. A. Wilkinson, of Cornell University (read by Professor W. D. Bancroft), were communicated and discussed, as printed in full in these Transactions. Mr. E. F. McElroy, of Albany, gave an interesting address upon the work of Joseph Henry, in Albany, in 1826-32.

The afternoon meeting was called to order at 2 o'clock, at the same place, President C. F. Burgess in the chair.

BUSINESS MEETING OF THE SOCIETY.

The reading of the minutes of the Twelfth General Meeting was dispensed with, and they were approved as published in the Transactions, Volume XII.

The report of the Board of Directors, including those of the

Secretary and Treasurer, was read by the Secretary and was accepted for publication in the minutes of the meeting, to which it is appended. (Mr. Carl Hering called attention to the anomoly, that the expenses of running the Society and printing and distributing its Transactions were nearly $7.00 per year per member, which was being accomplished on $5.00 annual dues.)

Dr. E. F. Wolff, of the Bureau of Standards, made a statement explaining the need of international action in the matter of selecting international electrical units, and read a letter from Dr. S. W. Stratton, of the Bureau of Standards, requesting the appointment of a committee to confer with committees appointed by the American Institute of Electrical Engineers and the American Physical Society, in reference to such standards. The Chair announced that the Board of Directors had already received this communication and acted upon it, recommending to the Society the appointment of a committee consisting of Carl Hering, *Chairman;* Prof. Th. W. Richards, Dr. Edward Weston and Prof. H. T. Barnes. On motion of Prof. J. W. Richards, duly seconded, the recommendation of the Board of Directors was adopted.

Mr. A. von Isakovics took the floor and related that a chemical manufacturer of New York City, desiring to have an electrochemical problem worked out, had conferred with him, and, on his advice, had decided to offer a prize for its solution. The following letter was the result, which was handed to the Secretary to be read to the Society:

(Abstract.)

"The Pacific Coast Borax Company would like to transmit a check for $500, payable to the Research Fund of the American Electrochemical Society, to be offered as a prize for the practical solution of the problem of making *Ferro-Boron* by a direct process from Borate of Lime (Colemanite). The decision of awarding the prize to be entirely in the hands of your Board.

"We will gladly furnish the necessary Borate of Lime, upon the certification of some officer of your Society, to any chemist who will seriously take up the subject of making these experiments."

On motion of Mr. Hering, amended by Mr. Isakovics, the proposition of the Pacific Coast Borax Company was accepted

with thanks, and our Board of Directors requested to formulate the details under which the award will be made.

Mr. A. von Isakovics, chairman of the Membership Committee, and Prof. A. T. Lincoln, a member of that committee, addressed the meeting upon the advisability of having junior associates connected with the Society, to accommodate in particular students who were, for the time, unable to pay the fee required for entrance into the Society. Such young men often have considerable interest in electrochemical work and the work of the Society, and if they could be attached in some way to the Society they would eventually form an important feeder to the full membership list of the Society.

On motion of Dr. W. R. Whitney, the matter of such a class of associates was referred to the Board of Directors for their consideration.

The tellers of the annual election presented the result of their canvas of the voting for president, three vice-presidents, three managers, treasurer and secretary, reading as follows:

Report of the Tellers of Election.

To the American Electrochemical Society.

Gentlemen: We have examined the ballots delivered to us by the Secretary, and report as follows:

Legal ballots	207
Invalid	1
Unidentified	4
Received late	5
Ineligible to vote	26
Total number cast	243

The results are as follows:

For President—E. C. Acheson, 171; W. R. Whitney, 21; C. A. Doremus, 9; S. P. Sadtler, 4; F. A. J. FitzGerald, 1; C. F. Reed, 1. Total 207.

For Vice-Presidents—C. P. Townsend, 158; C. A. Doremus, 139; W. R. Whitney, 115; W. D. Bancroft, 88; S. A. Tucker, 37; E. F. Roeber, 27; F. A. J. FitzGerald, 22; H. N. Potter, 19; H. R. Carveth, 1. Total 606.

For Managers—F. A. J. FitzGerald, 162; A. von Isakovics, 157; S. A. Tucker, 156; H. R. Carveth, 65; W. D. Bancroft, 46; W. R. Whitney, 3; E. F. Roeber, 2; C. P. Townsend, 1. Total 592.

For Treasurer—P. G. Salom, 199; F. A. J. FitzGerald, 1; Jos. W. Richards, 1. Total 201.

For Secretary—Jos. W. Richards, 201; F. A. J. FitzGerald, 1; P. G. Salom, 1. Total 203.

Yours very respectfully,

W. S. Franklin, *Chairman;*
A. G. Rau,
W. S. Landis.

The Chairman then declared as elected the following:

President (for one year)—Edward G. Acheson.

Vice-Presidents (for two years)—C. P. Townsend, C. A. Doremus, W. R. Whitney.

Managers (for three years)—F. A. J. FitzGerald, A. von Isakovics, S. A. Tucker.

Treasurer (for one year)—Pedro G. Salom.

Secretary (for one year)—Joseph W. Richards.

Prof. A. T. Lincoln, a member of the Membership Committee, took the floor to ask for consideration of the subject of associate membership. "In our universities there are many young men studying electrochemistry who would like to become members of this society, but the entrance fee, together with the annual dues, amount to a sum beyond what they can afford to pay. Most of them have considerable interest in electrochemical work and also in the work of the Society, and it would be well if there were some means of attaching these young men to the Society as associates."

Dr. W. R. Whitney moved that the matter brought up be refered to the Board of Directors for their consideration. Motion carried.

The business of the meeting being concluded, President Burgess called Past-President Carhart to the Chair, and delivered the Presidential address upon "The Corrosion of Iron from the

Electrochemical Standpoint," as is printed in full, with the discussion thereon, in the Transactions.

Papers on "Industrial Applications of Aluminum," by E. Blough, "Electrochemical Corrosion of the Rochester Steel Conduit," by Richard H. Gaines, and "Copper Cathodes in Chloride Solutions," by Saul Dushman, were read and discussed, as printed in full in the Transactions.

The evening session convened at 8.20 o'clock, in the same hall, Dr. W. D. Bancroft delivering a lecture on "The Electrochemistry of Light," followed by E. R. Taylor, on "Forestry, Water Storage, Power and Navigation," as printed in full in the Transactions.

An informal gathering in the cafe of the hotel, holding out until midnight, terminated the program of the day.

SESSION OF MAY 1st.

Special cars were taken from Albany, at 9 A. M., for Schenectady, arriving at Union University at 10 A. M.

The session was called to order at 10.15 A. M., in the Chemical Lecture Room of Union University. Dr. C. P. Steinmetz delivered a lecture on "Kinetic Molecular Energy," which was discussed at length, followed by papers on "The Heat of Vaporizations of Metals and other Substances," by Jos. W. Richards; "Electrochemical Patents," by A. B. Marvin, Jr.; "The Electrical Testing of Iron During Annealing," by E. E. F. Creighton; "Robert Hare's Electric Furnace," by C. A. Doremus (read by title); "The Synthesis of Hydrocyanic Acid in the Electric Furnace," by R. S. Hutton and E. W. Smith, and "Power for Electrochemical Industries," by J. Meyer (read by the Secretary), as printed in full in the Transactions. The meeting then adjourned.

The Taylor Instrument Company displayed in operation, in a room adjoining the place of meeting, a variety of pyrometers for measuring high temperatures, which were inspected with interest by many of those present.

The members and guests then took cars to the works of the General Electric Company, where they were first invited to lunch as guests of the company, afterward photographed, and then conducted in small parties through the various departments

of the enormous plant. Four hours were thus spent at the works, with great pleasure and profit to everybody attending. At 5.30 cars were taken back to Albany.

At 7.30 P. M., eighty-five members and guests sat down to dinner in a private dining room of the Hotel Ten Eyck, and later enjoyed many pleasant after dinner talks from various officers, prominent members and guests present.

SESSION OF MAY 2d.

The meeting was called to order by President C. F. Burgess, in the Chemical Lecture Room of the Rensselaer Polytechnic Institute, Troy, N. Y., at 10 A. M. Papers on "The Alloying of Iron and Calcium," by A. Hirsch and J. Aston (read by C. F. Burgess); "The Preparation of Calcium Alloys for Aluminothermic Work," by O. P. Watts and J. M. Breckenridge (read by O. P. Watts); "Conduction in Electrolytes," by L. Kahlenberg; "The Passage of Direct Current through Electrolytes without the Use of Electrodes," by Carl Hering; "Reversed Electrolysis," by J. W. Turrentine (read by Dr. W. D. Bancroft); "The Use of Dry Cells in Ignition Service," by J. W. Brown; "The Electrolytic Corrosion of Aluminum Bronze," by W. S. Rowland (presented in abstract by W. D. Bancroft); "Additional Experiments on the Electrolytic Corrosion of the Brasses," by A. T. Lincoln and G. C. Bartells; "The Electrolytic Refining of Iron," by E. F. Kern (abstracted by President Burgess); "The Conversion of Iron Pyrites, FeS^2, into a Magnetic Form," by O. L. Kowalke (abstracted by President Burgess); "The Nature of the Surface Film formed on Aluminum and Magnesium, and the Aluminum-Magnesium Cell," by H. T. Barnes and G. W. Shearer (read by the Secretary), were presented and discussed, as printed in full in the Transactions.

Mr. Carl Hering then moved a vote of thanks of the Society to the following firms and individuals, for the parts which each contributed towards the entertainment of the Society and the success of the Thirteenth General Meeting:

The General Electric Company.
The authorities of Union University.
The authorities of Rensselaer Polytechnic Institute.
The West Virginia Paper and Pulp Company.

The Hargreaves-Bird Company, of London, England.
The W. & L. E. Gurley Instrument Company.
The Burden Iron Works.
The Earl & Wilson Company.
The Commandant of Watervliet Arsenal.
The Local Committee of the Society.
The motion was carried unanimously .

President C. F. Burgess then called to the chair, President-elect E. G. Acheson, who addressed the meeting as follows:

"Fellow members of the American Electrochemical Society: I appreciate very highly the honor you have conferred upon me in electing me to the Presidential Chair, and I accept the honor and accompanying trust with the hope that I may not disappoint you.

"A few friends saw fit recently to make statements in a published letter of a kind that might have caused some of my brother members to have expected unusual results from me, but I assure you that any results which I may achieve, during my occupancy of the presidency of this Society, will be free from all miracle.

"My ambition is that our Society may continue to maintain the high standard it has attained under my predecessors. In order to maintain the advanced position we have taken in the world, it is essential that the membership give a loyal and earnest support to the Society, not only by attendance at its meetings, but by a liberal contribution to its Transactions. A man's value and the position that he attains in the world is not determined so much by what is in him as what proceeds from him. Many men fear to take a public position, dreading that they may endanger their commercial interests, and certainly if they have any important work in hand, their first effort should be to obtain the protection that is to be secured, to a certain extent, by our patent laws; but after that has been done I believe that increased security may be obtained by publicity. I have found in my experience that the public as a whole is trustworthy and just. To take aside one, two or three, and impart your knowledge to them, endangers your interests, but it it not so when you take the public into your confidence. We heard yesterday in the discussion on Mr. Marvin's paper of the possible security attainable

under our patent laws. It is not very favorable. But if that be supplemented by taking the public into your confidence, as I say, you will find it to support you and sustain you in your position, and it is a courageous man who will attack you, when protected in this manner.

"Among us we undoubtedly have many who are holding in secret a knowledge that may be of immense importance to their fellow members, our Society and the world at large. Can we not induce them to come forth and contribute information to our Transactions, and through them to the world at large. They will advance not only the interests of our Society, but of every secret a knowledge that may be of immense importance to their experiences, and, not only their successes, but their failures. Publication of failures have a value—it does not necessarily redound to a man's discredit, because he has made a failure, if he has made an earnest effort to accomplish results the world would be better for. Mr. Edison once told me that every experiment was a success, whether it accomplished the result you were seeking for or did not. It showed you what to avoid or what course to pursue.

"May I not ask you, during the period of my incumbency, to assist the further advancement of the Society, which has already attained a position which is to be envied by all bodies of a similar character." (Applause.)

The meeting was then adjourned.

After lunch, at the Rensselaer Inn, in which sixty-eight participated, about forty members and guests took train to Mechanicville, where an hour was spent inspecting the plant of the Duncan Paper Mill, of the West Virginia Paper and Pulp Company, and (by special permission of the Hargreaves-Bird Company, received the day previous,) the electrolytic chlorine and soda plant run in connection with it. The visit was highly interesting to all participants.

Returning to Troy, a number visited the scientific instrument plant of W. and L. E. Gurley's Sons, while others visited other points and places of interest in Troy.

Thus concluded one of the most profitable, interesting and enjoyable meetings in the history of the Society.

ANNUAL REPORT OF THE BOARD OF DIRECTORS.

To the Members of the American Electrochemical Society:

We submit herewith the annual reports of the Secretary and the Treasurer for the year 1907, the former containing the detailed financial statements of receipts and expenditures.

The increase in number of members was satisfactory, and there is every evidence that the rate of gain of membership, which was over 10 per cent., will be maintained during 1908.

The financial status shows expenditures slightly larger than receipts, but there are modifying circumstances which, if taken into account, would really show a balance in the other direction. There is no cause at all for concern, as the situation is well in hand and improving.

The following are the more important actions taken during the year by the Board of Directors:

Prof. S. A. Tucker was elected to the Board, also Mr. F. J. Tone and Mr. F. A. J. FitzGerald, all as Managers, to fill unexpired terms caused by the resignation of one member of the Board and the election of two others to fill other offices.

An appropriation was made to cover the cost of translating Mr. Gin's memoir on "The Rare Metals," which had been awarded the Frenzel prize, by the Society, with a view to publishing it in the Transactions. The first section, on "Molybdenum," has already been published in Volume XII., and the next, on "Tungsten," is to appear in Volume XIII.

On the transfer of the Secretaryship to Prof. Jos. W. Richards, at Lehigh University, South Bethlehem, Pa., the authorities of the University placed at the disposal of the Society, rent free, a commodious room on the ground floor of one of the University buildings, opening directly upon a driveway; for which liberality the University was duly given the thanks of the Board.

The financial condition of the Society, as shown by the reports of the Treasurer and Secretary, may be summed up in the statement that receipts and expenses are practically equal. There is a reserve in form of bonds of two thousand dollars on hand to cover any future excesses of expenses above receipts, and there are on hand nearly five thousand volumes of back volumes of Transactions, representing a cost of about five thousand dollars,

and a possible asset, when all sold, of ten thousand dollars. Since the sales of back volumes is increasing, it is probable that realization on this asset will be of important financial assistance to the Society in the future. The offer of 25 per cent. discount to members purchasing the back volumes necessary to complete their sets has resulted in many members now possessing complete sets of the Transactions.

The Society still needs the active co-operation of each and every member in increasing our membership, and in contributing according to his ability and opportunity to the publication of electrochemical literature.

The holding of the Autumn meeting in New York City appears so successful that it may well be considered as an annual feature. The Fourteenth General Meeting will be held in New York City, in October next.

CHAS. F. BURGESS, *President.*
JOSEPH W. RICHARDS, *Secretary.*

Albany, April 30, 1908.

SECRETARY'S ANNUAL REPORT.

To the Board of Directors of the American Electrochemical Society.

GENTLEMEN: The report of my predecessor, Mr. S. S. Sadtler, printed in Volume XI. of our Transactions, was dated May 1, 1906, to May 2, 1907. Since the date of our Spring meeting is movable, I think it better to make the Secretary's report cover the calendar year, so as to coincide with the fiscal year of the Society.

In 1907 the Society held two general meetings, one in Philadelphia, May 2, 3 and 4, and one in New York City, October 17, 18 and 19.

In 1907 there were issued two volumes of Transactions. Vol. X. being those of the New York City meeting, of October 8 and 9, 1906, and Vol XI. those of the Philadelphia meeting, May 2-4, 1907. The Transactions of the New York City meeting, of October 17-19, 1907, were issued in April, 1908.

As before, the edition of each volume of Transactions has consisted of 1,000 copies, bound in cloth, for distribution to our members; 50 extra copies, in sheets, for distribution to authors of papers, and 500 copies, bound in paper, about half of which are sent to the Faraday Society and the rest remain in stock.

There were on hand, December 31, 1907:

Volume.	Bound in cloth.	Bound in paper.	Total.
I	306	...	306
II	330	...	330
III	232	...	232
IV	245	240	485
V	210	228	438
VI	227	233	460
VII	236	244	480
VIII	271	247	518
IX	239	251	490
X	346	256	600
XI	258	257	515
			4,854

Number of volumes sold during 1907 191

Condition of the Society in regard to membership:

Members January 1, 1907		620
Elected and qualified as members in 1907		80
Reinstated		9
		709
Resignations	19	
Deaths	3	
Dropped for non-payment of dues	3	
		25
Members December 31, 1907		684

Financial Statement.

January 1, 1907, to December 31, 1907.

RECEIPTS.

Entrance fees	$ 400 00
Annual dues	3,235 50
Advertising	355 86
Sales of Publications	439 67
Interest	111 62
Cash difference on re-investing funds	50 54
By clerical error in 1906 accounts	5 00
Membership certificates	7 96
Type metal sold to printer	21 68
	$4,627 83

EXPENDITURES.

Salaries	$ 963 58
Office expenses	433 43
Printing, stationery and postage	794 20
Publications (Volumes X and XI)	1,970 69
Commissions on advertising	155 50
Moving and storage	59 75
Meetings of Society	320 18
Appropriation to New York Section	100 00
Insurance	36 60
Refund of dues of member dismissed	5 00
	$4,838 93

CASH ASSETS, JANUARY 1, 1907.

Cash balance, Jan. 1, 1907—On deposit	$ 318 94
In cash box	50 00
Bonds held by the Society (cost price)	1,988 75
	$2,357 69

CASH ASSETS, DECEMBER 31, 1907.

Cash balance, December 31, 1907	$ 157 84
Bonds held by the Society (cost price)	1,948 75
	$2,106 59
Loss in cash assets for the year 1907	$ 251 10

The loss in assets is rather apparent than real, since an inspection of the records for 1906 shows some $700 of 1907 dues paid in December, 1906, and credited to that year, while only about

half that sum of dues of 1908 were paid in December, 1907. The Society really received more money applicable to 1907 expenses than the expenses of 1907. It will be the endeavor of the Secretary to collect as much as possible of back dues and current dues, and not to solicit or depend upon this advance payment of dues in December. On the whole, income and expenses properly chargeable to 1907 came near to balancing, so as to give little, if any, cause for anxiety.

It is hoped that by making a systematic canvas of our members a considerable sum may be netted from the sale of back volumes. Our present stock of Transactions represents a cost of about $5,000, and a selling value of nearly $10,000. The Society will realize upon this more and more from year to year, and it is certain to become a regular yearly asset of great assistance to our finances.

The membership increased a net 64 in the year, with prospects of a still greater gain in 1908; the membership April 30, 1908, is now 715, a gain of 31 in four months. Our foreign membership alone is now over 100, and the increase in interest in our Society abroad is a most satisfactory indication and guarantee of our permanent progress.

JOSEPH W. RICHARDS,
Secretary.

Lehigh University, South Bethlehem, Pa.,
April 30, 1908.

TREASURER'S ANNUAL REPORT.

FOR THE YEAR 1907.

Balance, January 1, 1907	$ 318 94	
Receipts from S. S. Sadtler, Jan. 1, 1907, to April 30, 1907	2,541 59	
Receipts from Joseph W. Richards, May 1, 1907, to Dec. 31, 1907	2,136 24	
		$4,996 77
Expenditures, Jan. 1, 1907, to Dec. 31, 1907, as per list		4,838 93
Balance, December 31, 1907		$ 157 84

PEDRO G. SALOM,
Treasurer.

Members Elected and Qualified.

January 28, 1908.

J. Robert McFarlin, Electrochemical Engineer, Electric Service Supplies Co., Keokuk, Iowa. Res.: 18 North Eleventh Street.

James Aston, Manager, Thos. Aston & Son, Milwaukee, Wis. Res.: Twenty-fourth Avenue and South Pierce Street.

George E. Long, Graduate Student, University of Wisconsin, Madison, Wis. Res.:1124 West Johnson Street.

Rudolph Albrecht, Chemist, The Sun Co., Marcus Hook, Pa.

George R. Kendall, Lecturer in Chemistry, McGill University College, Vancouver, B. C. Res.: 1629 Comox Street.

Edward Zaremba, Manager, American Foundry and Machine Co., 945 Monadnock Bldg., Chicago, Ill. Res.: 1220 Wilton Avenue.

Otto Mantius, Engineer, American Foundry and Machine Co., 945 Monadnock Bldg., Chicago, Ill. Res.: Hotel Vendome.

Johan Fr. Irgens, Managing Electrical Engineer, Technisk Bureau, Limited, Walkendorffsgade 12, Bergen, Norway.

Walter H. Aldridge, Consulting Engineer, Canadian Pacific Railway, Trail, British Columbia.

February 29, 1908.

Herbert C. Jennison, Testing Laboratory, Coe Brass Mfg. Co., Ansonia, Conn. (P. O. Box 313.)

Percy A. Boeck, Chemist, Norton Emery Co., Worcester, Mass.

Wm. C. Marti, Student, University of Illinois, Urbana, Ill. Res.: 210 East Clark Street, Champaign, Ill.

March 25, 1908.

Louis E. Ward, Experimental Laboratory, Dow Chemical Co., Midland, Mich. Res.: Fort Atkinson, Wis.

Dr. G. Baborovsky, Docent in the Chemical Institute, University of Prague, Prague, Bohemia. Res.: Sokolsko Str. 16.

S. T. Hauser, Jr., Secretary, Missouri River Power Co., Helena, Mont.

April 30, 1908.

Maurice L. Dolt, Instructor in Chemistry, Brown University, Providence, R. I.

William L. Spalding, Superintendent, Electrolytic Refinery; Buffalo Smelting Works, N. Y. Res.: 1 Austin Street.

Paul R. Manahan, Manager, Peabody Branch, Avery Chemical Co., Peabody, Mass. Res.: 37 Caller Street.

Oscar R. Foster, Chemist, The De La Vergne Machine Co., 549 Monroe Street, Brooklyn, N. Y. Res.: 304 Alexander Avenue, Bronx, New York City.

John A. Yunck, General Electric Co., Harrison, N. J. Res.: 422 Meeker Street, South Orange, N. J.

W. C. Slade, Department of Chemistry, Brown University, Providence, R. I. Res.: 76 Comstock Avenue.

May 30, 1908.

W. R. Clymer, Superintendent, National Carbon Company, Cleveland, Ohio. Res.: 1426 West One Hundred and Seventh Street.

William C. Bray, Instructor, Massachusetts Institute of Technology, Boston, Mass. Res.: Room 16, Eng. C.

Henry D. Hibbard, Consulting Engineer, 144 East Seventh Street, Plainfield, N. J.

C. M. Fitz Gerald, 170 Nassau Street, New York City.

An address delivered at the Thirteenth General Meeting of the American Electrochemical Society, held at Albany, N. Y., April 30, 1908; Past President H. S. Carhart, LL. D., in the Chair.

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[PRESIDENTIAL ADDRESS.]

THE CORROSION OF IRON FROM THE ELECTROCHEMICAL STANDPOINT.

By C. F. Burgess.

Depreciation is a subject which is to-day occupying the attention of financiers, economists and accountants. It is one which presents various phases, none of which is more important than those of obsolescence and physical decay. For one of these the engineer may be held responsible; the other he should work to prevent. Obsolescence comes as a direct result of new discoveries in science and their adaptation to man's use. Physical decay apparently follows the working out of nature's processes, yet it has been proved possible for the scientist and engineer largely to reduce the rapidity with which such decay progresses.

In the use of iron as the most important structural material, attention has been given hitherto more to design and erection than to preservation, but as the amount of erected iron increases, the importance of preserving it likewise increases. The older our existing iron structures become, the greater is the need of retarding their decay.

The phenomenon physical decay of iron and its alloys has long been known, but is little understood. To control it, a deeper knowledge of the underlying causes is necessary. When we recognize the fact that iron structures depreciate annually in value through physical decay at a rate varying from perhaps one per cent. to twenty or more per cent., we have a means of stating the importance of this in money units. When viewed from the standpoint of safety to life, as well as that of preservation of property, the matter takes on a far greater significance.

The importance of this subject from economic, socialistic, governmental and humanitarian standpoints should be sufficient

to enlist interest in the work, quite aside from the fascination which it exerts in itself. As Sir Roberts Austen has said: "The study of metals possessess an irresistible charm for us quite apart from its vast national importance. Metals have been sadly misunderstood; in the belief that animate beings are more interesting experimenters have neglected metals, while no form of matter in which life can be recognized is thought to be too humble to receive encouragement. Bacteria with repulsive attributes and criminal instincts are petted and watched with solicitude and comprehensive schemes are worked out for their development and culture."

It is not difficult to show that methods which have proved so fruitful in results when applied to the study of living things are singularly applicable to metals and alloys, which really present close analogies to living organisms. Their anatomy, the structure and framework, are being studied under the microscope, their biology and pathology by means of the pyrometer and various other devices. Thus do we study power of endurance, effect of stress, and recovery from fatigue when allowed to rest.

Corrosion of iron may be considered as the generic term covering a number of diseases peculiar to iron and iron alloys. So little is understood as to the causes of even the most common of these diseases that to prescribe for them requires considerable assurance on the part of the experimenter. There is an insistent demand at the present time for further experimental study of corrosion and for the gathering of accurate records on corrosion phenomena.

Some of our leading authorities hold that primarily iron corrosion is an electrolytic phenomenon. Such a view was advanced by W. R. Whitney (Journal Am. Chemical Society, 1903, p. 394), and this was corroborated and notably extended by W. H. Walker (Journal Am. Chem. Soc., 1906, p. 1251). A. S. Cushman, through some interesting experiments described to our society last year, also sought to ascribe corrosion to electrolytic action.

The acceptance of such a belief would place upon the electrochemist the first responsibility of making a thorough study of iron corrosion, and it is certainly true that such research would offer him a most attractive field for work.

In viewing corrosion of iron as an electrochemical action, it may be desirable to divide into classes various kinds of corrosion encountered in practice. The first class to be considered is:

Corrosion of Underground Structures.

It is well known that under normal conditions iron pipes buried in the earth for distribution of gas and water will corrode so slowly that the life may well exceed a century. The owners of such pipes were greatly disturbed not many years ago to find that a disease had been contracted by their pipes, presumably through association with electric railways. They attempted, and are still attempting, to demonstrate to the courts that the railway companies are responsible for damage caused to their pipes by the leakage of currents from the railway returns.

It has been shown beyond doubt that current flowing from iron to earth subjects the iron to electrolytic corrosion, but beyond discovering methods for mitigating the destruction, the electrochemist has not succeeded in freeing from electrolytic trouble pipes located near a single-trolley railway.

This phenomenon has attracted such attention that to many people the term "electrolysis" is synonymous with destruction of underground pipes. In spite of extensive study which has been given to this matter it is interesting to note various curious beliefs which are held even by some of these experts. Thus we have the disputed point as to whether current flowing from iron to earth will cause a quantitative corrosion as required by Faraday's laws; some hold that the earth conducts to a certain degree metallically and therefore a small current density may not cause any corrosion whatever; while others assert, and probably more correctly, that Faraday's laws hold exactly for large and small currents alike. Testimony has been given to the effect that the flow of current through the earth results in the deposition of a coat of iron upon pebbles in the earth, a phenomenon certainly of interest to those who have experienced the difficulty of depositing iron under most favorable conditions upon a conducting cathode. The statement is repeatedly made that current flowing from the rails to the pipes does not produce electrolysis, but

that current flowing in the reverse direction is dangerous. This, of course, is only another case of "whose bull is gored."

In the study of this type of corrosion the electrochemist is called upon to clear up erroneous beliefs by quantitative measurements. So far remedies applied have been qualitative rather than quantitative, and before accurate work can be done in treating this trouble a large amount of data must be made available; such as the specific electrolytic conductivity of various earths—clays, gravels, etc. The minimum electromotive force for flow of current must be more carefully studied to determine whether an electromotive force, no matter how small, will cause electrolysis, or whether polarization is to be counted upon.

Some authorities assert that if the direction of the flow of current can be reversed occasionally the electrolytic corrosion of both electrodes may be prevented, the argument being that current flowing from the iron will carry iron in a solution and that some iron will be redeposited when the direction of the current is reversed. This remedy has been attempted in the operation of certain electric railways by reversal of the polarity of the generators once a day, or every hour, or even more frequently, and the observations made during such practice led to the conclusion that the more frequently the reversals are made the less is the danger from electrolysis. In fact, when we carry this practice to its extreme limit and have a reversal several times a second we arrive at alternating current transmission, the advent of which is generally assumed will be an absolute cure of electrolytic troubles, although some experts assert that an alternating current system of distribution will not remedy present difficulties. The writer's experience in depositing iron from a solution even under the most favorable laboratory conditions has led him to believe that the chance conditions to be met with in the earth are not unlikely to make it possible to deposit iron from the earth on to the metallic electrode. Consequently relief from an occasional reversal of the current does not appear practical of attainment. This statement may not apply, perhaps, when the frequency of reversals is so rapid as to make the current come under the classification of alternating current.

Galvanic Action.

Iron in contact with a metallically conductive material electronegative to itself, and both making contact with an electrolyte, constitute an active electrochemical system in which the iron is subject to corrosion. The rate of corrosion depends upon the electromotive force, upon the conductivity of the electrolytic and metallic conductors, and upon the polarization. If the electrolyte is such that the hydrogen is liberated on the electronegative surface it may produce polarization sufficient to stop the flow of current. If a depolarizing material be present the polarization will be decreased and the increased current thereby produced results in increased rate of corrosion. (Walker, et al; Journal Am. Chemical Society, 1906, p. 1251).

As examples of an electrochemical system of this type, the following well known case may be named: An iron ship in a harbor with a copper sheathed ship are considered undesirable companions, since if metallic contact be made between the two, the iron suffers by being made the anode of a huge electrochemical system of which the copper ship is the cathode and the sea water the electrolyte. It is not good practice to attach a bronze propeller on a steel shaft of sea-going ships, for unless suitable protective steps are taken the neighboring steel will be damaged.

The more electronegative the material the more marked is the electrolytic action, and some forms of conductive carbon have properties such as to make the electrolytic action particularly pronounced. Various investigators have pointed out that carbon cinder imbedded in an iron surface, or carbon making contact with iron in any way engenders corrosion by galvanic action. This action takes place whether the piece of iron is of large or small size and the kind of action produced by particles of microscopic size is identical with that produced by the large particles. The uncombined carbon which chemical analysis shows to exist in certain kinds of iron may therefore increase the corrodibility of such iron. The measurement of the single potential of iron sulphide shows this to be electronegative to iron and its presence in iron will give rise to active couples. It can hardly be doubted that such surface exposing spots of iron sulphide is one upon which electrolytic action will take place if an electrolyte be present.

Almost any microphotograph of iron and its alloys shows non-uniformity of composition of surface exposed to corrosion, and we are justified in the belief that the micrographic constituents should be studied in dealing with iron corrosion from the electrochemical standpoint. We do not know in what electrochemical order the ferrite, pearlite, cementite and other constituents of iron alloys may arrange themselves. Data as to the single potential of these various constituents are needed if we would express quantitatively the tendency of a certain combination to corrosion. At the present time our only knowledge of these potentials is of a qualitative kind and also very fragmentary. The available published data come from the records of the work done by the metallographists in their microscopic study of iron. Highly polished iron surfaces have been treated with various corroding acids and reagents, the purposes being to corrode the different constituents at different rates to make the outlines of the various materials apparent under the microscope. A study of the literature on metallography for the purpose of classifying these observations might constitute interesting and valuable work.

It is perhaps doubtful if the exact measurement of any one constituent could be made, at least, with the present methods of measurement, since in measuring the electrical potential of an iron or iron alloy, a value is obtained which may be the electromotive force given by the most positive constituent, or it may be that produced by the polarization phenomenon, or it may be some intermediate or composite value. W. H. Walker and associates (Journal of Am. Chem. Soc., Sept., 1907) have devised an ingenious method for determining the different potentials established by different portions of an iron surface, and they have shown "that in certain instances areas having marked difference in potential exist in far greater number upon the surface of a piece of iron prone to corrosion than upon iron which is resistant to corrosion." Whether this method would lend itself to the measurement of microscopic portions of an iron surface is problematical. An active electrochemical system can usually be detected wherever corrosion is observed, but whether corrosion can exist where no electrolytic action is possible is a matter which appears far more difficult to determine.

Assuming a similarity in chemical composition and metallo-

graphic constitution in different samples of iron or iron alloys, the question may be asked, "Can the single potential differ in different specimens or different parts of the same specimen?" The conditions which have been suggested under which differences of potential of this sort may be produced are those resulting from *mechanical working* or deformation of a metal, and by *inequality of temperature.*

Influence of Strain on Corrodibility.

Does strain in iron increase tendency to corrosion? This is a question which has been the subject of interesting discussion and upon which there is radical difference of opinion. Data obtained by different investigators are quite contrary, and it is natural then that contradictory conclusions have been drawn.

In referring to those radically different conclusions of different experimenters the writer disavows any desire to enter into a controversy. But it appears that unless errors which are allowed to creep into methods of measurement are recognized and then guarded against, the data obtained can be of little value, and these errors can perhaps be detected by comparison of the methods employed by different observers.

As a matter of scientific interest we may refer to that well-known riddle which runs as follows: Two steel clock springs are identical as to weight and quality of material, and differ only in that one of the springs is coiled and the other uncoiled. These are immersed in an acid solution and completely dissolved. What has become of the energy which was stored up in the coiled spring? The answer which most easily suggests itself is that this energy must have been liberated during the chemical process of solution, and manifesting itself as heat. Upon this supposition, in dissolving the coiled spring, more heat would be liberated than in dissolving the uncoiled spring. Further, the coiled spring would be more chemically active, and if so this chemical activity should be manifest as increased electrical contact potential existing between the metal and the solvent.

There are many instances coming under practical observation which seem to bear out the idea that a metal under strain is more subject to a dissolving or corroding action than is unstrained

metal, this relation being particularly true in iron and its alloys. Mr. James Andrews, in 1894 (Proceedings of the Institution of Civil Engineers), described some experiments by which he attempted to demonstrate that strained iron has a higher potential in a corroding solution than has unstrained. He concluded, however, from the results of his measurements, that the *reverse* condition holds, and that unstrained metal is more rapidly acted upon by the solution than the strained metal. Mr. Carl Hambuechen, in 1900 (Bulletin of the University of Wisconsin, Engineers' Series), pursued an investigation which was, in a measure, a duplicate of that made by Mr. Andrews, with the exception that Hambuechen sought to eliminate some error in the former work by modifications and refinements in the method of measurement. He produced experimental data showing that the iron behaved as it should according to theory, and in fact, he was able to secure, in some cases, a remarkable similarity of stress-electromotive force diagrams with the stress-strain diagrams obtained simultaneously on the sample. He says "the application of stress to metal causes an increase in chemical activity, this increase being especially marked after the elastic limit has been reached."

In 1906, T. W. Richards and G. E. Behr, Jr., contributed a paper to the Carnegie Institution of Washington, Publication No. 61, entitled "The Electromotive Force of Iron Under Varying Conditions and the Effect of Occluded Hydrogen." This paper asserts the presence of regrettable errors in Hambuechen's work, and among the conclusions it is stated that "Measurements of the free energy change in iron during a pull upon wire great enough to cause rupture gave results showing that this change must be very small." The authors apparently conclude from their work that the changes in electromotive force actually produced are too small and the data too scanty and irregular to warrant conclusions of value from being drawn. This view apparently places some of Hambuechen's data under the charge of accidentally falling into a systematic order, which order would not have been shown had the alleged errors been avoided.

In 1907, Messrs. W. H. Walker and Colby Dill discussed "The Effect of Stress Upon the Electromotive Force of Soft Iron" before the American Electrochemical Society. In their

summary the statement is made that "the magnitude of the potential suffered by soft iron when tested in a tension machine below the elastic limit is exceedingly small. . . . The change, when great enough to be measured, was negative: the strained metal had a slightly lower potential than the same metal unstrained. . . . Somewhere above the elastic limit the potential rises suddenly several hundredths of a volt."

It may perhaps be not unprofitable to enter into a consideration of the cause of the marked differences of the results obtained by different observers and the diametrically opposite conclusions which were drawn therefrom. Of the various authorities mentioned, Hambuechen has apparently secured results which uphold that plausible theory that iron upon which mechanical work has been done retains some of the energy in a potentialized form capable of being measured by electromotive force readings. The other authorities discredit these results. It is probable that none of the results referred to have been obtained under conditions which are free from all sources of error. Hambuechen's work was done under the supervision of the writer, who therefore feels justified in discussing some criticism of his methods and conclusions. Mr. Hambuechen pointed out in his bulletin that chances for error existed in Andrews' work by reason of the fact that the surfaces whose potential was being measured were not protected from action of the air. He devised a cup-shaped arrangement which surrounded the sample of iron in the testing machine and carefully protected all of the parts of the iron from the air and the electrolyte except such portion of the surface as was being immersed in the electrolyte and whose potential was being measured. He recognized that the amount of potential changes were exceedingly small and that the potential established by a metal in contact with an electrolyte is easily upset by the flow of exceedingly small amounts of current. The use of an ordinary galvanometer used in connection with the compensation method was believed to allow the flow of sufficient current to materially polarize the small surface under measurement. He therefore used a capillary electrometer, which acts as a condenser of small capacity and does not allow the steady flow of current through it. This electrometer had a sensitiveness of .0007 of a volt, and in addition to this sensitive-

ness it was unaffected by vibration and magnetic disturbances and could be mounted in close proximity to the testing machine.

Messrs. Richards and Behr employed a d'Arsonval galvanometer sensitive to 0.001 volt, and they apparently did believe it necessary to guard fully against polarization phenomena. Walker and Dill likewise took this view as to the precautions deemed necessary, for they employed a d'Arsonval galvanometer of fairly high resistance, but provided with a shunt "to protect the galvanometer from too heavy currents during the preliminary adjustment of the resistances."

In both papers referred to, that by Richards and Behr, and by Walker and Dill, objection is made to Hambuechen's results on account of his use of ferric chloride as the electrolyte against which the potential of the iron was determined. The former writers say that "this unfortunate choice" (of ferric chloride) "completely invalidates all the results. The reason is very simple. Ferric chloride is always hydrolized to a considerable extent—that is, it contains acid. * * * There exists in the electrolyte a continually changing concentration of ferric, ferrous and hydrogen ions and reliable work is out of the question. The effect of these influences combined would cause the electromotive force to change steadily, quite independently of any stress and strain effects." Data are given showing that in two cases the electromotive force of iron rose 0.192 and 0.123 volts in about seventeen hours, and they say that this rise would have been ascribed by Hambuechen to strain.

While it is perhaps true that a solution better than ferric chloride might be chosen, the criticism of Hambuechen's work for this reason is perhaps too severe, since he did recognize the fact that the electromotive force was subject to change, regardless of any strain effect. The change becomes so slow after a half-hour that a stress-strain diagram could be run through in a sufficiently short time that the natural change would have little effect in masking the changes produced by strains. In fact, in producing the autographic record of the stress-strain diagrams, Figure I, the testing machine was run continuously and the electromotive force measurements had to be taken with some rapidity. The writer believes that these observations of varying electromotive force are more probably the results of potentialized

energy in the iron than the effects of hydrolysis of the ferric chloride solution, as emphasized by Richards and Behr.

The feature which at first sight might discredit more than any other the accuracy of Hambuechen's results is that he found changes in electromotive force which were materially greater than those calculated on the assumption that all of the energy applied to an iron rod in pulling it apart is thereby potentialized.

Barus has studied the disposition of energy applied in rupturing a piece of iron. ("The Energy Potentialized in Permanent Changes of Molecular Configuration," U. S. Geological Survey

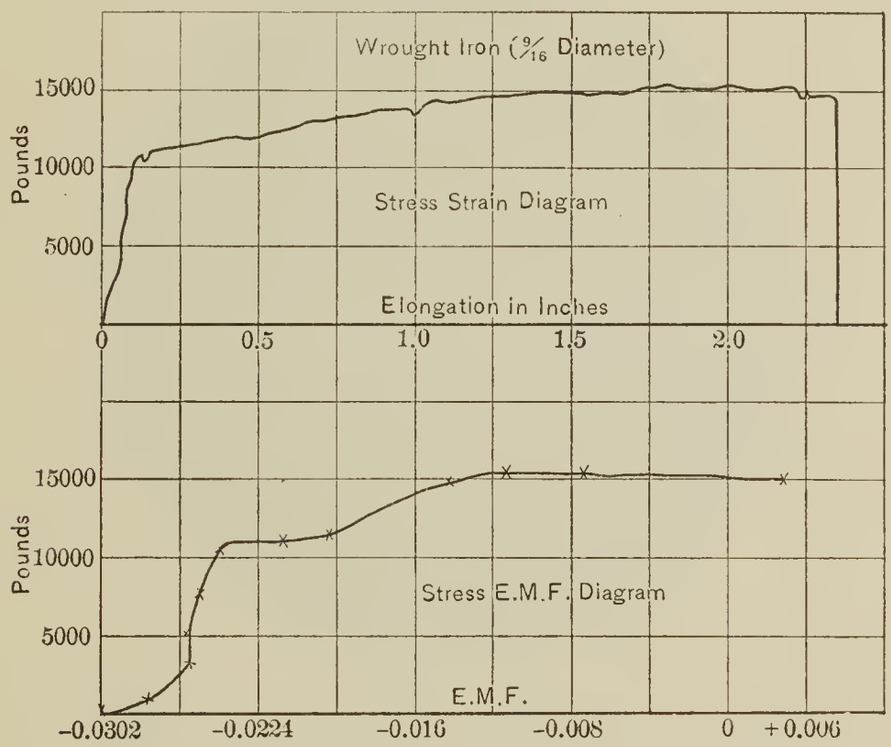

FIG. 1.
Stress-strain and Stress-E.M.F. Diagrams on Wrought Iron.

Bulletin, No. 94, 1892), and quoting from him we read: "To summarize, it appears that as much as one-half of the work done in stretching up to the limit of rupture may be stored up permanently." Calculation of the increase of electromotive force by the potentializing of energy in iron involves the application of the formula

$$E = \frac{W \times c}{96540 \times g}$$

where

E is increase of electromotive force in volts.

W is energy stored, expressed in Watts-seconds.
c is the chemical equivalent.
g is weight in grams of the iron in which the energy is stored.

From measurements of stress and deformation Hambuechen calculated that the possible increase in electromotive force on a particular sample was .0126 volt (on the erroneous assumption that *all* of the applied energy was potentialized). He found in some of his measurements values two or three times as high as were apparently theoretically possible, to explain which he assumed an excessive storing of energy in the outer layer of iron as compared with that at the center. Richards and Behr were justified in considering this an erroneous assumption. They have apparently overlooked the possibility, however, of a non-uniform distribution of such energy as may be potentialized by strain, for in their calculations of electromotive force they have assumed the energy to be equally stored in all particles of the sample of iron.

Ewing and Rosenhain, in a paper on "The Crystalline Structure of Metals" (Phil. Trans., Royal Soc., Vol. CXCIII), have given results of miscroscopic study on the effect of strain on metals. Figure II. shows the results of strain in Swedish iron, the black lines through the grains being slip-bands. It is well-established in their work that the influence of strain is not uniformly distributed throughout the mass. It appears that the shape of the grains is altered, but that the crystals making up the grains are not deformed. "The conception that metals adapt themselves to the new shapes imposed upon them when they undergo plastic deformation by means of slips along cleavage or gliding planes within each crystalline grain, leads naturally to the supposition that the crystalline elements themsleves undergo no deformation in the process."

Energy is expended in overcoming the adherence or attractive force between crystals, and if there is a storage of this energy it might well be considered as being stored in the portion of metal adjacent to these surfaces. As this metal containing potentialized energy is exposed to the electrolyte, the electromotive force of this portion will be greater than that of the remaining portions. To calculate this electromotive force according to the formula

157539

given requires a knowledge of the actual weight of that portion of the metal in which the energy is stored, which obviously would be less than that obtained by weighing the entire mass. This weight is, of course, impossible to determine by known methods of measurement.

The electromotive force of the most electropositive particles is then greater than the *average* electromotive force calculated. The question then arises as to which value—the maximum, the minimum or average value, or some value of over-voltage of hydrogen, is obtained by experimental measurement of con-

FIG. 2.
Strained Swedish Iron, Magnified 300 Diameters.

tact potential. Richards and Behr have described their determination of the single potential of small globules of iron around which were wrapped platinum wires to make contact. Their voltages are given as being the values for iron even though it is in contact with the more electronegative platinum. Likewise we have in a zinc amalgam the electromotive force of the zinc almost unaffected by the electronegative mercury. From analogy we might expect, therefore, that the potential would be that set up by the most electropositive particles on its surface. And if this line of reasoning is correct, we can easily explain why Hambuechen's measured values of electromotive force were higher than

those calculated, and we may perhaps wonder why the differences were not even greater than found.

It should be recognized, in comparing the results of different investigators, that the materials designated as iron may, in fact, be different grades of iron. Richards and Behr confined their attention to highly purified iron, while Hambuechen used the term more loosely as designating the commercial grades of the metal. He found that the increase of potential by strain is more marked in steel than in pure iron, and a microphotograph of steel reveals the presence of various constituents. In all probability there is a difference in the storage of energy in the various constituents, and consequently the possibility of higher electromotive forces.

It may be emphasized again, and in this connection, that the microscope is a useful device in studying the phenomena pertaining to the corrodibility of iron.

Additional Experiments Showing Corrodibility of Strained Iron.

As bearing upon the question whether strained iron has a greater tendency to corrode than the unstrained metal, the following experimental observations may be of interest. These are abstracted from a compilation of results recently obtained by John Thickens, in the Applied Electrochemistry Laboratory of the University of Wisconsin, and also from work carried on under a grant from the Carnegie Institution.

Test rods of mild steel were treated as follows: The rods, 8″ long and ¾″ in diameter, were turned down at the middle section for a length of ⅜″ to a diameter of ½″. These were subjected to a stress in a testing machine until the elastic limit had been exceeded and the narrow portion had necked down to a diameter of about 0.4″. The entire bars were then turned down to uniform diameter, this being done under running cold water to prevent heating. Bars 3″ long were cut from the central portion of the longer bars, and including the strained portion. Some of these bars were subjected to corrosion by suspension in dilute hydrochloric acid solutions, and others by making them the anode in neutral solutions of ammonium chloride, and causing current to flow under low current density. In all cases a marked difference was noted in the rate at which the

strained portions corroded as compared with the unstrained, and although the sample looked absolutely uniform before corrosion the decrease in diameter of the strained portion after corrosion is marked. Some of these specimens before and after corrosion are shown in Figure 3.

Differences of potential of from 5 to 9 millivolts were noted between two electrodes, one of which constituted the strained portion and one the unstrained.

Another set of samples were strained beyond the elastic limit

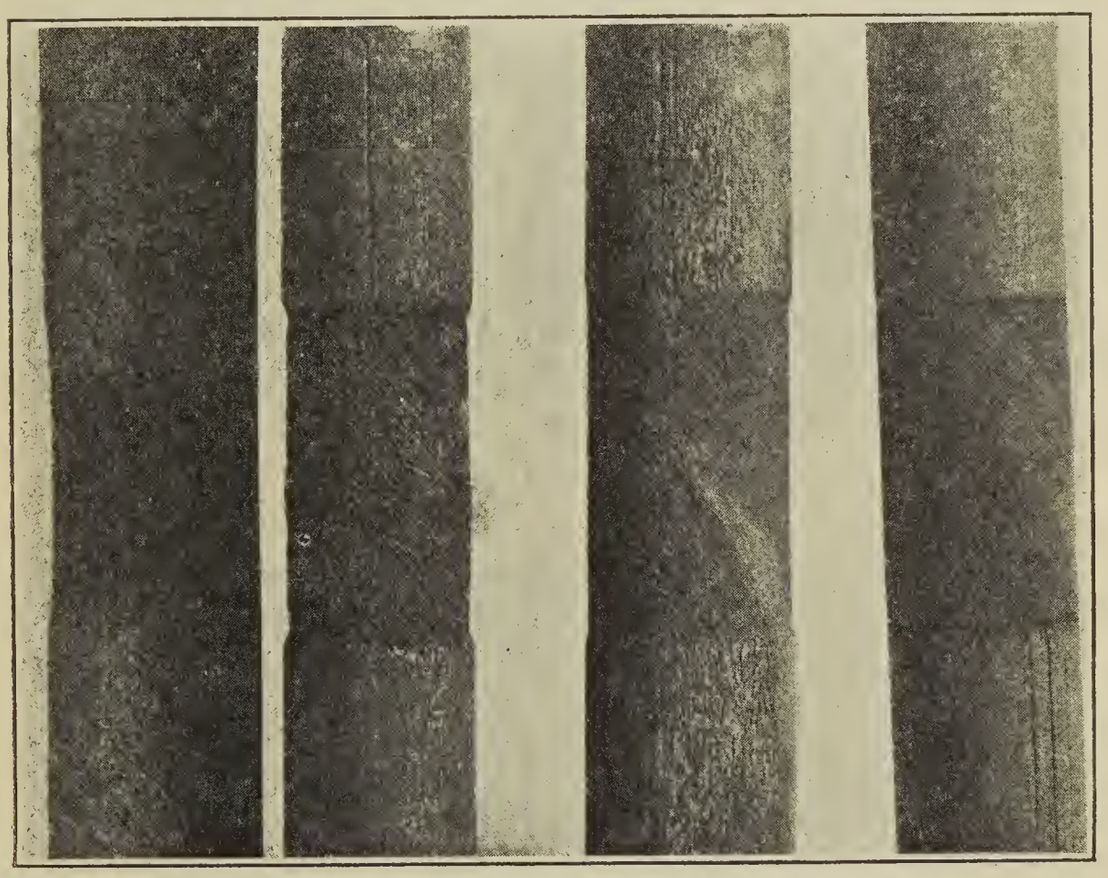

FIG. 3. FIG. 4.

FIG. 3.—Mild Steel Tension Specimen, Corroded Electrolytically 263 Hours 0.04 amperes.
FIG. 4.—Mild Steel Specimens, Strained by Torsion and Corroded.

by torsion. The original bars were 3″ x 1″ x 1″; they were turned down for a length of one inch at the center to a diameter of ⅝″, the ends being left square. They were subjected to a torsion through 180°, after which the entire length was turned down to a uniform diameter, the specimen in this condition having a uniform appearance on the entire surface. Three grades of iron were employed, and are designated by the terms wrought iron,

mild steel and electrolytic iron. The last one was prepared from electrolytic iron which had been melted and forged.

These were subjected to corrosion by suspension in dilute acids, as well as by making them the anode in neutral solutions and corroding electrolytically, using a low current density. In all cases a greater corrodibility of the strained metal was noted, as shown by the reduction in diameter, as well as by the general appearance of the corroded surfaces. The greatest difference was noted in the mild steel, it was less marked in the wrought iron, and least with the electrolytic iron. The results of some of these tests are shown in Figure 4.

The more rapid electrolytic corrosion of the strained portion appears to be due to the fact that the strained metal is electropositive to the unstrained, the current finding the easier path through the surface of the electropositive metal. Another phenomenon which points to the fact that the strained metal is the more electropositive is noted in immersing the machined test samples in dilute hydrochloric acid. There is a liberation of hydrogen bubbles on the unstrained portion. This is not a temporary condition, but it persists, and indicates that there is electrolytic action, the strained portion serving as the anode and the unstrained as the cathode. It was noted that the purer the iron, the less pronounced is the phenomenon, and in the case of the electrolytic iron, the corrosion as well as the distribution of the evolved hydrogen bubbles was nearly uniform. Figure 5 shows non-uniform distribution of the hydrogen bubbles.

The effect of annealing a previously strained bar was noted by heating a machined bar imbedded in iron filings to a temperature of 900° F. for five hours. The difference in corrodibility between the strained and unstrained portions was then shown to have been completely eliminated by this treatment. In the dilute acid solutions the distribution of the hydrogen bubbles was uniform.

An instance where the increased corrodibility of steel is a matter of practical importance is in the use of punched metal. It is a universal specification in boiler construction that the rivet holes shall be drilled and not made by the cheaper method of punching. The reason for this is that the former method gives

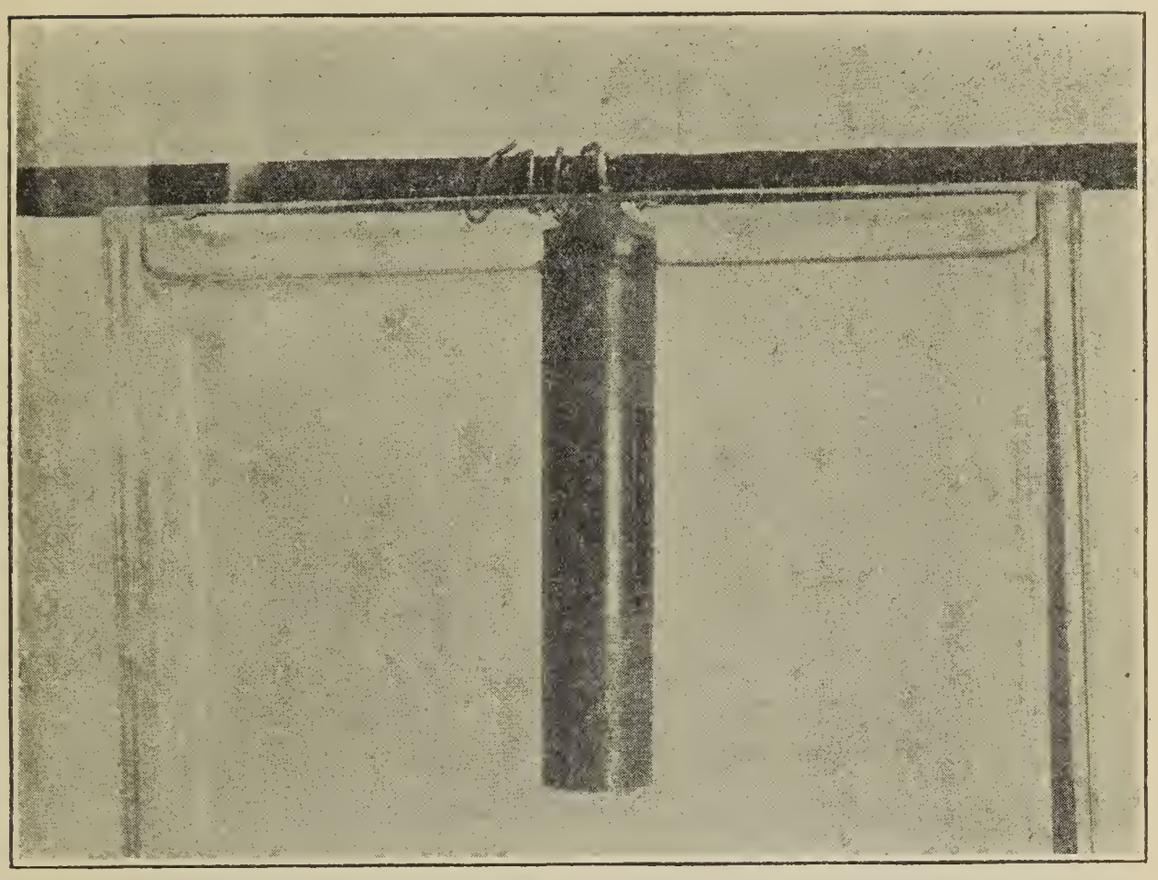

FIG. 5.
Hydrogen Bubbles on Strained Specimens.

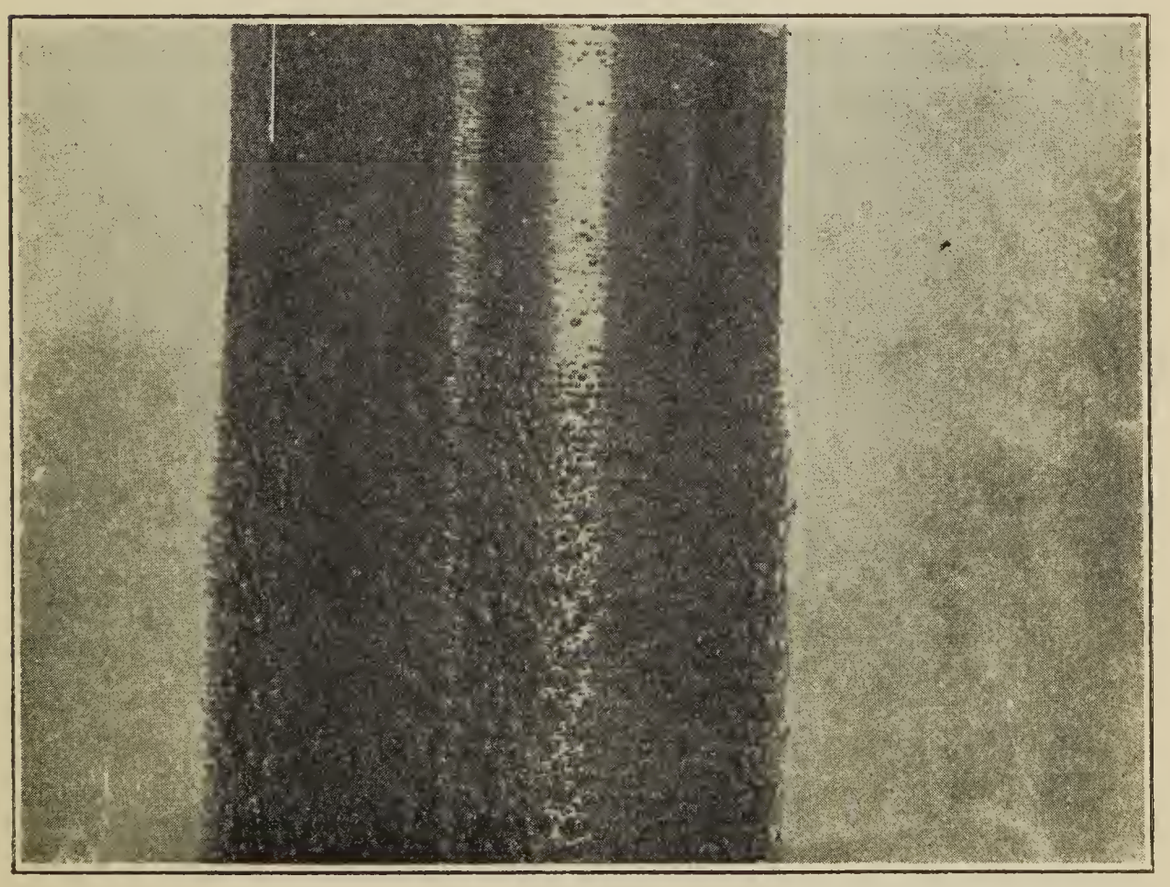

FIG. 5A.
Same as Fig 5, Magnified.

better results as far as durability and freedom from corrosion is concerned. In addition to the liability of cracking or otherwise mechanically damaging the metal surrounding the punched hole, it has been found that rivets inserted in punched holes tend to become loose and leaky.

In the process of punching, straining both by compression and tension is produced, the punched disc being compressed, and the walls of the hole and the disc having been subjected to tension of shearing. According to those who hold that unstrained metal is more subject to corrosion than the strained, the corrosion around a punched rivet hole will proceed some distance away from the hole; on the other hand, if it is true that the strained portion is electropositive to the unstrained, then the metal nearest the hole should corrode the more rapidly. This is a matter which is capable of settlement by experimental demonstration, and the following experiments were carried out with this object in view.

Some steel plates ¾″ thick were punched cold, the punchings having a diameter of 1″. The punched plates were subjected to corrosion, both electrolytic and by dilute acids. It was noted that the corrosion was most rapid on the sides of the hole and in the immediate vicinity.

Figure 6 shows one of a number of plates which had been etched electrolytically, and acid etching produces a similar effect. This photograph does not clearly show the corrosion inside the punched hole, but it shows that the effect of the strain extends some distance, nearly two inches from the hole. The curved grooving, radiating from the center, is taken by the observer as indicating the lines of strain in the surrounding metal. .

Some of the punchings were attached to wires and suspended in various corroding solutions. The suspension wires and the point of contact with the iron pieces were protected from the solution by paraffine. It was shown that the sides of the cylinders had a far greater rate of corrosion than had the circular surfaces, as illustrated in Figure 7.

One of the punchings, and a piece of similar size cut from the original steel plate, were suspended as electrodes in a ¼ normal HCl solution and connected to a mil-ammeter. The current was constant at about ½ milampere for several days, the punching

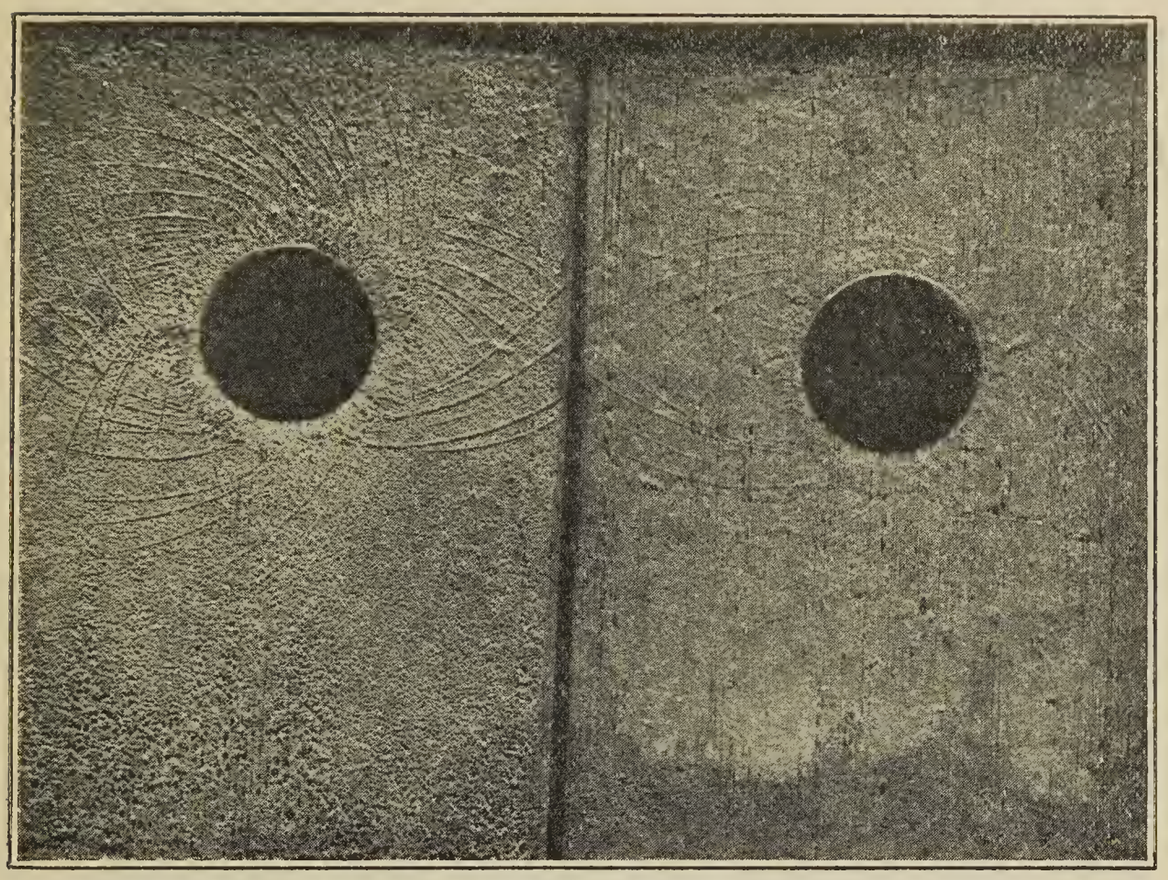

Fig. 6.
Corrosion of Punched Boiler Plate.

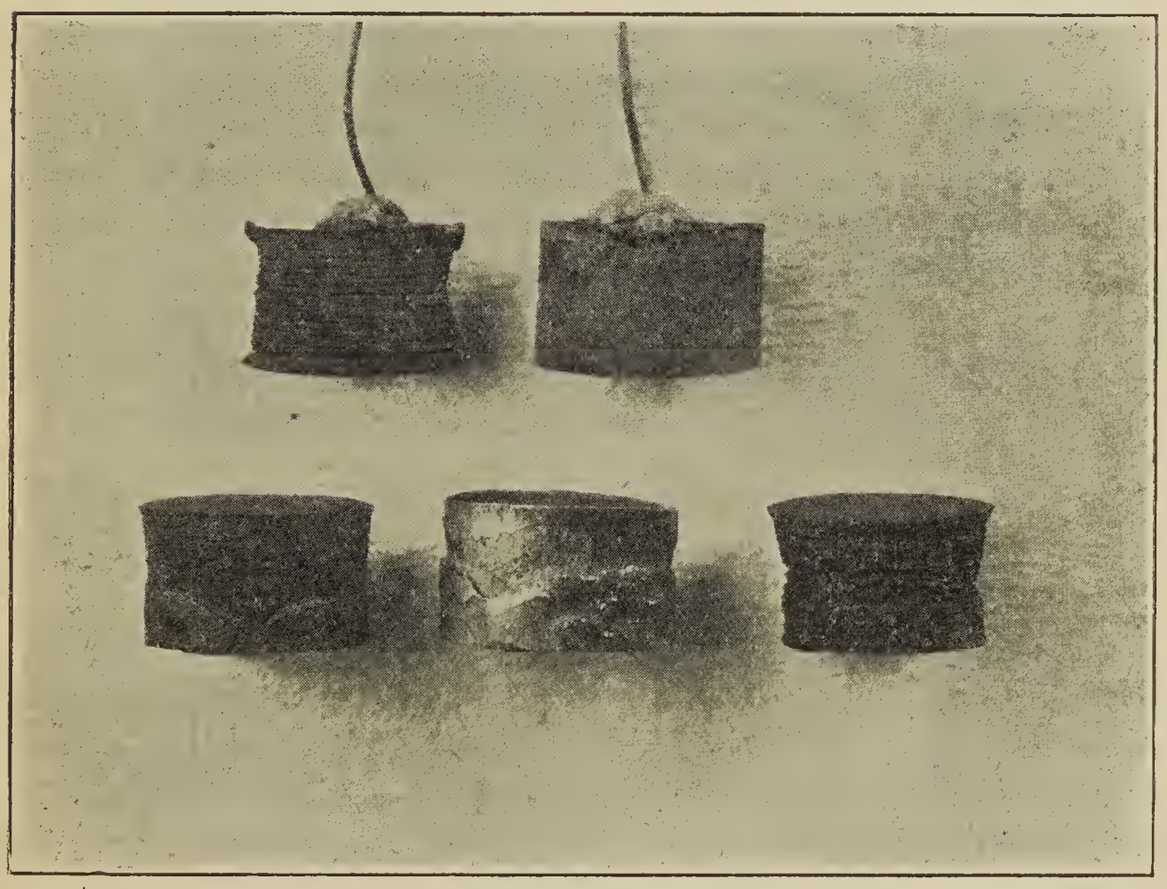

Fig. 7.
Corrosion of Punchings.

being the anode, and corroding the more rapidly. Similar results were obtained by immersing in a normal KCl solution, the current remaining constant at 0.75 mil-amperes. In both solutions it was noted that on first immersion the current was much higher than the constant value subsequently maintained, this decrease being due to polarization as manifested by an accumulation of hydrogen on the unstrained cathode.

Upon momentarily lifting the two electrodes into contact with the air, and again immersing, the flow of current greatly increased. By blowing air through the solution a similar result was attained, and by adding a very small quantity of sodium peroxide the current quickly rose from 0.75 mil-amperes to over 30 mil-amperes. The effect of oxygen in all of these cases was apparently due to its depolarizing action on the cathode, which allowed more current to flow, and which consequently increased the corrosion of the strained metal anode. This appears to be in confirmation of the important discovery made by W. H. Walker, that oxygen causes oxidation, not by uniting with the iron, but by depolarizing, and allowing other corrosive agents to become active.

The experiments which have just been described are qualitative rather than quantitative, but show in an apparently conclusive manner that strained metal *does* have a greater solution tension than the unstrained. The results are of technical as well as of scientific interest, and the effects are so pronounced that it appears obvious that our available methods of measuring the differences of potential between strained and unstrained iron when properly applied should yield accurate quantitative data. Further quantitative measurements appear to be desired.

Influence of Inequalities of Temperature Upon the Corrosion of Iron.

As bearing upon the influence of temperature upon the corrodibility of iron, there are presented here the results of some work carried on by Mr. S. G. Engle and the writer. These results are more fully described in a thesis by Mr. S. G. Engle, entitled "The Influence of Inequalities of Temperature Upon the Corrosion of Iron." This investigation was originally taken up

in connection with the study of certain peculiar corrosion pheomena which are commonly found in locomotive boilers.

To one familiar with the corrosion produced by stray currents in underground pipes, the pitting and grooving of boiler tubes has the appearance of being electrolytic action. A place where corrosion is particularly noticeable in locomotive boilers is just inside the end shells where the tube is expanded. At one end of the boiler a copper shim is placed between the tube and the end plate, the purpose being to utilize the ductility of the copper in making a tight joint. At the other end the tube is expanded directly to fill the hole in the end plate. If copper shims were used at both ends of the tubes a logical explanation of the fact that tubes corrode in the immediate neighborhood would be that a voltaic couple is set up between the copper and the iron. It appears, however, that the corrosion is just as marked at the end where copper is not used, and other explanation must therefore prevail. The one most commonly accepted is that the iron tube on being expanded is thereby strained and this strained metal corrodes more rapidly than does the neighboring unstrained metal. There is not enough data to absolutely fix this point.

There is also an irregular pitting in the tubes, the rapidity of the action depending upon the care taken of the boiler, upon the kind of feed water used and perhaps upon other factors. Among the results of this kind of corrosion is the frequent puncture of the tubes, the extinguishing of the fire, the stalling of trains between stations and the retirement from commission of valuable machinery. The pitting may be somewhat general in distribution, but usually there are a few deep pits with the surrounding metal apparently intact. It is a matter of general observation that the pitting is more marked on the tubes nearer the shell of the boiler, rather than on those farther toward the interior—in fact, the interior tubes may last as long as several sets of tubes renewed on the lower row. This is explained commonly by the supposition that the circulation of water, also the introduction of fresh feed water, is such as to emphasize corrosive action.

The object of the investigation previously referred to was to determine if possible whether the equivalent of galvanic cells is established in locomotive boilers, due to inequalities of tempera-

ture in the different portions. The most highly heated metal in the boiler are the tubes which are exposed to the hottest products of combustion. The lower tiers of heated tubes are probably subjected to this heat. The direction of the flow of heat is from the interior of these tubes to the water which in turn is in contact with the cooler shell of the boiler. If the boiler tube is, by being hotter, rendered more electropositive than the boiler shell, we would expect a galvanic action resulting in the corrosion of the tube. We would expect the corrosion to be at such places as the current finds the most ready path between the anode and the cathode. The shortest path between the hot anode and the cooler cathode would be between the lower and the side tubes and the interior of the boiler shell.

TABLE I.

Time.	Temp.	Contact Potential.
4.17	20 C.	0.085
4.19		0.064
4.21		0.070
4.23		0.085
3.25		0.085
4.30		0.102
4.35		0.114
4.40		0.143
4.45	38	0.143
4.50		0.150
4.55	38½	0.143
5.00		0.158
5.05	39½	0.165
5.10	41	0.172
5.15	42	0.172
5.20	42	0.187
5.21	42	0.187
5.22	42	0.187*
5.23	42	0.187
5.25	42	0.202
5.28	41	0.202
5.38	37½	0.202
5.44	34½	0.202
5.50	32	0.202
5.55	31	0.202

* Heating current cut off.

Tests were first made to determine the effect of heating of the single potential of iron. It has been previously noted by various authorities that a slight heating does not appreciably

change the electromotive force of iron. The purpose of these experiments was to determine what electromotive force changes take place when there is a high rate of transfer of heat from the iron to water. An iron ring was immersed in water contained in a glass dish. The ring was heated by currents induced by a solenoid placed below. The ring acted as a one-turn secondary of the transformer. The purpose of this method of heating was to avoid trouble of introducing heat by conduction through terminals passing through the walls of the containing vessel or through the surface of the solution.

TABLE II.

Time.	Temp.	Contact Potential.
3.15	21° ½ C.	0.085
3.18	21 ½	0.085*
3.20	33	0.106
3.25	50	0.137
3.30	61	0.165
3.35	71	0.188
3.40	79	0.203
3.45	82	0.225
3.50	84	0.240
3.55	85	0.246†
4.10	71	0.246
4.15	86	0.250
4.20	94	0.262
4.25	95	0.276
4.30	96	0.276
4.35	96	0.276‡
4.40	79	0.268
4.50	53	0.232
5.00	43	0.224
5.10	37	0.218
5.25	32 ½	0.212
5.30	31 ½	0.212
5.32	31	0.144**
5.33	30 ½	0.202
5.34		0.212

* Began the test.
† Took the burner away for four minutes.
‡ Turned the lamp out.
** Took this reading directly after shaking the solution.

The water used was that taken from a locomotive boiler, and had a specific resistance of 332 ohms at 23.2° C. Measurements were made by comparison against the normal electrode having the assumed value of -.56 of a volt, the method of measurement being similar to the Oswald Potentiometer Method.

Table I gives the results of one series of measurements, being one of three runs. The results of each of these were almost identical. The maximum temperature was 42° C., it being impossible to go beyond that value on account of the limited current capacity of the solenoid which was used.

In another test the dish containing the ring immersed in water was heated by means of a burner placed below it. The results of this are given in Table II. These data also show the fall of potential during the cooling.

An interesting peculiarity in the electrical heating is shown in the decrease of potential which is first produced by the heating and the subsequent rise after the minimum point has been reached. This minimum was not observed in the test where the external heat was applied.

It was desired to carry the temperatures of the iron surface beyond that which was possible by the former methods of heating, and this was accomplished by bending a soft iron wire into a "U" shape, immersing it in the water and heating it by the passage of an alternating current through it. Voltage readings were taken between this electrode and another one of the same material which was not heated by the passage of the current. It was found that there were certain irregularities in the measurements, due to the fact that the wire dipped down through the surface of the electrolyte. This was remedied by passing the wires out through the bottom of the vessel, which contained an asbestos stopper. Water taken from the locomotive boiler was again used as the electrolyte. It was found that the heated wire first became more electropositive, then became steadily negative as the heating progressed, until the wire became fused. This tendency for the heated wire to become negative in this case is ascribed to the fact that the wire became hot enough to oxidize when in contact with the water, coating itself with the more electronegative iron oxide.

Another experiment consisted in using two steel tubes of similar composition, one tube being one inch in diameter and the other four inches. The inner tube was fastened through a rubber stopper passing through an inverted glass jar, above which rested the larger iron tube. The joint between the glass bottle and the large iron tube was closed by means of a cement

joint. A Bunsen burner was placed inside the inner tube and served to heat this metal. Electrical connections were made between the lower part of the tube extending below the stopper and outside of the iron jacket. Locomotive boiler water again was used as the electrolyte between these tubes. The results of one of these tests are given in Table III. Instead of measuring the electromotive force between these tubes, connection was made through a milli-ampere meter to determine the

TABLE III.

Time.	Amperes.	
12.20	—0.0009	Inner tube anode.
12.30	—0.0020	
12.40	—0.0026	
2.54	—0.0026	Began the test.
2.55	—0.0032	
2.56	—0.0035	
2.58	—0.0045	
2.59	—0.0050	
3.00	—0.0055	
3.05	—0.0091	
3.10	—0.0115	
3.13	—0.0123	
3.15	—0.0123	Water boils. Put in more water.
3.20	—0.0105	
3.25	—0.0100	Water boils freely.
3.30	—0.0075	
3.35	—0.0060	
3.40	—0.0045	
3.45	—0.0040	
3.49	—0.0027	
4.06	—0.0027	
4.25	—0.0026	
4.45	—0.0026	Turned gas off.
4.45½	—0.0028	
5.05	—0.0010	
5.40	—0.0004	

amount of current which flows under the conditions given. It was to be noted in these tests that the inner tube was the anode, and therefore the one to be corroded; also that the corrosion current increases as the diameter increases until the water begins to boil. It is to be noted that after the maximum current has been reached the current begins to decrease slowly. This increase of current to a maximum and its subsequent decrease, regardless of the fact that the temperature conditions are maintained, is a characteristic which has been noted in many experi-

ments, and it appears that the flow of current produces an increase of resistance, either on the electrode surfaces or in the electrolyte itself, which serves to increase the amount of current flowing. This is merely a suggestion, and the explanation of it requires further study.

The experiments thus far indicate decided tendency for a heated surface to become electropositive, as compared with the cooler piece of metal in the same solution. This is a condition which may exist in locomotive and other boilers, although direct conclusions could not be drawn from these experiments without recognizing the fact that these were carried out under atmo-

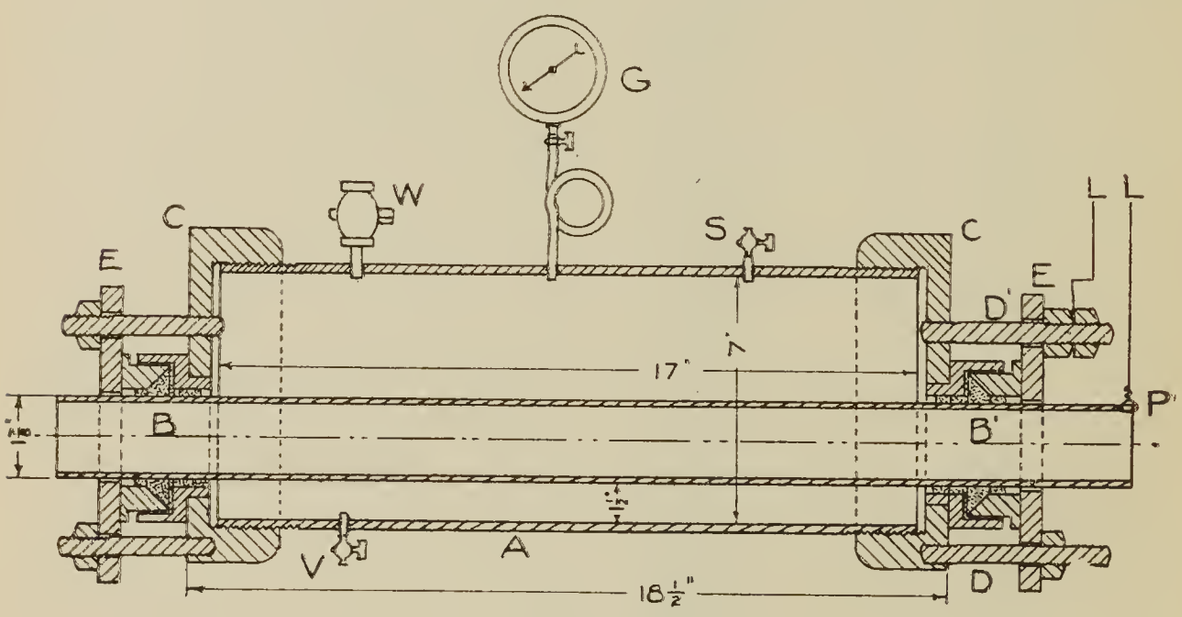

Fig. 8.
Apparatus for Studying Boiler Corrosion.

spheric conditions, while the water in a boiler is usually under high pressure.

To conduct laboratory tests upon conditions which would more clearly approach the conditions found in a locomotive boiler, an apparatus, as illustrated in Figure 8, was constructed. This consisted of an iron pipe "A," 7 inches in diameter, and 17 inches long, closed by iron caps screwed on the ends. "B" and "B¹" are stuffing boxes placed below the center of the caps through which the pipe "P" passes. The purpose of this stuffing box is to insulate the pipe from the steel cylinder, at the same time allowing this joint to stand a high steam pressure. Asbestos packing was found to serve this purpose admirably. The

cylinder was fitted with a steam gauge and steam cock for the release of pressure, and another opening for the introduction and drawing off of water and sediment. Heat was applied to the apparatus by means of a blast flame inside of the smaller tube. The interior of the apparatus was first thoroughly boiled in caustic solution and rinsed in water.

Electrical connections were made between the inside and outside tubes through the electrical measuring instruments consisting of mil-ammeter and mil-voltmeter. A large number of tests were made by means of this apparatus, employing various

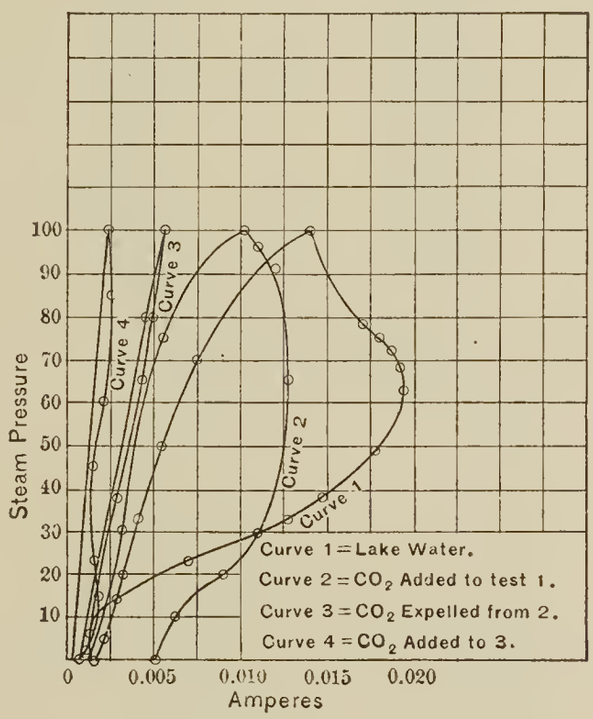

FIG. 9.
Corrosion Curves in Steam Boiler.

kinds of boiler water and operating under a variety of conditions as regards pressure, rapidity of heating, cleaning out of the apparatus, etc.

In each of the runs the apparatus was first completely filled with water and then 2½ pints of solution were withdrawn in order that the same amount of liquid and air space be present each time. As an illustration of some of the data obtained by this device, reference may be made to Curves 1, 2, 3 and 4, Figure 9, showing graphically the data recorded in Tables IV., V., VI. and VII. These results are given, not for the purpose of describing completely this investigation referred to, but to call

Table IV.

Time.	Amperes.	Volts.	Lbs. Pressure.
3.25	—0.0012	—0.0003	0*
3.28	—0.0012	—0.0003	0†
3.30	—0.0014	—0.0003	0
3.35	—0.0012	—0.0002	0
3.40	—0.0020	—0.0004	0
3.45	—0.0070	—0.0014	14
3.50	—0.0128	—0.0025	33
3.55	—0.0148	—0.0036	49
4.00	—0.0192	—0.0039	63
4.01	—0.0192	—0.0039	68
4.02	—0.0189	—0.0038	72
4.04	—0.0180	—0.0036	75
4.05	—0.0170	—0.0034	78
4.10	—0.0140	—0.0028	100‡
4.20	—0.0076	—0.0016	70
4.30	—0.0055	—0.0012	50§
4.35	—0.0041	—0.0008	33
4.40	—0.0032	—0.0007	20
5.05	—0.0018	—0.0004	5

* Heated tube anode.
† Began test.
‡ Gas off.
§ Opened steam cock.

Table V.

Time.	Amperes.	Volts.	Lbs Pressure.
9.15	—0.0012	—0.0003	0*
9.20	—0.0012	—0.0003	0†
9.22	—0.0010	—0.0002	0
9.25	—0.0032	—0.0007	0
9.30	—0.0050	—0.0010	0
9.35	—0.0063	—0.0011	10
9.40	—0.0090	—0.0014	20
9.45	—0.0110	—0.0016	30
9.50	—0.0122	—0.0017	50
10.00	—0.0120	—0.0017	91
10.01	—0.0120	—0.0015	96
10.02	—0.0102	—0.0013	100‡
10.05	—0.0055	—0.0010	75
10.10	—0.0036	—0.0014	32
10.18	—0.0012	—0.0002	0

* Heated tube anode.
† Began test.
‡ Turned gas out. Opened steam cock to let CO_2 and pressure off.

TABLE VI.

Time.	Amperes.	Volts.	Lbs. Pressure.
10.18	0.0012	0.0002	0*
10.21	—0.0015	—0.0003	5
10.25	—0.0025	—0.0004	15
10.30	—0.0030	—0.0006	38
10.35	—0.0042	—0.0008	65
10.37	—0.0049	—0.0009	80
10.40	—0.0056	—0.0010	100†
10.45	—0.0047	—0.0008	80
11.45	—0.0008	—0.0001	0‡

* Continued test of Table No. 5, and water still hot.
† Turned Gas off.
‡ Opened the steam cock and the current went to 0.0010 (–).

TABLE VII.

Time.	Amperes.	Volts.	Lbs. Pressure.
2.45	—0.0016	—0.0004	0*
2.57	—0.0020	—0.0005	0
3.00	—0.0020	—0.0005	0†
3.01	—0.0008	—0.0002	0
3.01½	—0.0005	—0.00005	0
3.15	—0.0010	—0.0002	2
3.21	—0.0015	—0.0003	13
3.25	—0.0020	—0.0003	25
3.30	—0.0023	—0.0004	85
3.32	—0.0023	—0.0004	100‡
3.33	—0.0018	—0.0003	98
3.34	—0.0020	—0.0004	98
3.35	—0.0022	—0.0004	98
3.37	—0.0025	—0.0004	98
3.40	—0.0025	—0.0004	98
3.46	—0.0020	—0.0003	80
5.00	—0.0004	—0.00005	0

* Heated tube anode.
† Began test.
‡ Opened steam cock to regulate the pressure.

attention to this form of apparatus and method of investigation as a means for studying corrosive action of different kinds of boiler feed water. It is possible that measurements of this sort may be useful in determining the efficacy of various materials which may be used to improve boiler feed water and for getting quantitative as well as qualitative information regarding boiler corrosion.

Curve 1 was obtained by first cleaning out the apparatus and using lake water which had first been boiled and then saturated with oxygen by bubbling this gas through the water while in place in the testing apparatus. As the pressure increased, due to the application of heat, the current gradually increased up to a maximum of 19.2 milliamperes, with a corresponding open-circuit voltage of .0039 volts. This occurred at a pressure of about 68 pounds. The current and voltage then slowly decreased until at 100 pounds pressure the heat was turned off. The current curve on cooling is shown by means of the dotted lines. The introduction of the oxygen appeared to have a decided effect in increasing the amount of current and consequently the amount of corrosion.

While the pressure was decreasing during the cooling the steam cock was opened so as to allow the oxygen to be expelled from the water and from the gas space above it, and when completely cold the same solution was saturated with carbon dioxide, likewise filling the gas space above the water. Another run similar to the former was then made, Curve 2 giving the results. If conclusions might be drawn from this data they would be to the effect that the presence of oxygen has a greater influence than has the presence of carbon dioxide in promoting the corrosive action. To compare the corrosive action in the solution as used in the last test to the same solution freed from carbon dioxide, this gas was expelled by opening the steam cock while the apparatus was under a certain amount of pressure. Another run was made on this same solution by again applying heat and raising the pressure to a hundred pounds. Results are given in Curve 3. Curve 4 shows the subsequent test on the same solution through which carbon dioxide had again been passed, and this in turn showed apparently that the carbon dioxide has practically no influence on the corrosion current.

The effects of the addition of various other dissolved substances were observed; thus treating lake water with one gram of soda ash per 5 gallons of water, a method commonly employed for treating boiler feed water, gave potentials in the *opposite* direction, the heated tube being the cathode. This same result was found in a more pronounced way by increasing the percentage of soda ash. However, with a solution obtained from a

locomotive boiler which had been treated with soda ash and in which the soda ash had been concentrated by repeated evaporation, the inner tube became the anode. The heated tube was likewise found to be the anode when using 1 gram of magnesium sulphate or magnesium chloride per gallon. Barium hydrate, caustic soda, dilute acids and other materials were used, but the results need not be given here in full.

It was always noted that no matter what electrolyte was used, the current gradually increased to a certain point and then decreased. It was also noted that in repeating tests without otherwise changing the solution, the successive results always gave lower values of current and pressures. In other words, a fresh solution always causes apparently a higher current and more corrosion than one which has been used. This would coincide with the general belief that it is the fresh feed water in boilers which has the greatest corrosive action. This fact, and the one that each curve shows the current to reach a maximum, after which it decreases—even if the heat be kept constant—requires an explanation. Among the suggested explanations is the influence of the formation of a high resistance coating on either the anode or the cathode, formed from the corrosion products, and a second factor might be the partial decomposition of the electrolyte or a decrease of such materials in the electrolyte which might promote corrosion. For example, the presence of oxygen acts as a depolarizer at the cathode and facilitates the flow of current as long as there is any oxygen present. It is natural to expect, therefore, that as the oxygen in the boiler water is eliminated, either by escaping with the steam or uniting chemically with other materials, the polarization will increase, and consequently the measured voltage and current will decrease.

That both these factors apply in part should undoubtedly be recognized. From the testing apparatus the tube was removed at frequent intervals and in all cases a coating of more or less adherent scum or incipient scale was observed. Upon removing this and again making the test an increased current was noted. An examination of the surface of the tube after various runs revealed the fact that the corrosion had not been uniform but was in the form of pits which could be readily distinguished by the naked eye.

W. H. Walker has given us his opinion that the presence of oxygen in a solution promotes corrosion by acting as a depolarizer and in this way allows a more ready passage of galvanic or corroding currents. His views can undoubtedly find confirmation in the study of boiler corrosion, for it has been repeatedly noted that water which has been thoroughly saturated with air and consequently with oxygen, is especially corrosive when used as feed water. In fact, some of the most injurious cases of corrosion can be found where distilled water is used—distilled water having been allowed to become saturated with oxygen from the air.

The question naturally arises, "Do the currents, as measured in the tests referred to, reach a sufficiently large value to indicate a serious amount of corrosion?" Various of the laboratory tests have shown current of .01 ampere. In 24 hours this is equivalent to a corrosion of ¼ gram of metal; and since this corrosion is not evenly distributed but is confined to a few localities, it is obvious that these laboratory experiments will give basis for the belief that pitting of locomotive boiler tubes is galvanic action, and that the galvanic action is sufficiently rapid to cause perforation of the tube in a few months, or weeks, or even days.

When we view the rapid deterioration of modern iron structures and at the same time call to mind that famous iron shaft at Delhi which has endured with practically no deterioration for a time dating back toward the beginning of the Christian era, we are perhaps led to wonder whether our efforts toward increasing the life of iron is a step toward the restoration of a lost art. But whether or not a non-corrodible iron has ever been produced, there is much reassurance that improvement will result from systematic and scientific study of corrosion phenomena.

Applied Electrochemistry Laboratories,
University of Wisconsin.

DISCUSSION.

MR. E. G. ACHESON: I would make a few remarks in regard to this paper. I think I can give some information bearing on the subject treated. I have found the presence of graphite in water would prevent the water from causing the steel to rust, but on removing the steel from that particular water and putting it into another quantity of clear water, it would rust. I had hoped to be able to cure the steel and prevent corrosion, but I found that continued soaking in the water would not affect it. Water containing defloculated graphite was proven to be an efficient compound for some purposes, as in screw cutting, where one could use the water and get the high specific heat of the water, in conjunction with the non-rusting quality of the graphite.

Recently I received a letter from a gentleman who was placing on the market a lapping machine. The machine, as described to me, was particularly designed for lapping shafting. He said very definitely in the letter that, after grinding a piece of shafting, the pores were all opened up, but that after lapping with deflocculated graphite for a period of five minutes there was a great difference between it and a piece of shafting that had not been treated in this manner. One would corrode in moist atmosphere and the other would not corrode. He did not tell me in what form he used the graphite, whether in oil or water, but I presume it was in water.

MR. R. H. GAINES: Is anything known of the composition of the shaft in India that seems to be perpetual?

PRESIDENT BURGESS: The composition is known, analyses having been published, but I do not remember what the results are.

MR. J. F. MCELROY: I want to add one word which may not be pertinent to this discussion, but at the same time may be of interest in connection with it.

I regard Prof. Burgess' paper as a most excellent one and as of great interest in showing how electrochemical effects are changed by the internal strains of the metals themselves. I have for some time been testing the conductive power of sheets of perforated iron with different styles of perforation. These sheets have been about 4″ wide and from 14 to 20 mils thick and carrying current of about 300 amperes. The results of these tests

seem to indicate that there is a zone around the hole in the perforated metal in which the metal is highly strained by the act of perforation and that the electrical resistance of the metal in this zone had been increased. Whilst my tests on this have not yet been completed, sufficient work has been done to show that in closely perforated metal the increase of resistance of the metal is greater than can be explained by the cross section and length of the path through the conducting perforated metal. In sheet metal with widely distributed perforations, I have not noticed this effect; but in closely perforated metal the increase is apparently 30% higher than what can be accounted for by the cross section of metal and length of the conducting path through it.

Dr. F. A. Wolff: Could not the effect last described be accounted for by a change in the shape of the cross-section. The average cross-section would not determine the resistance, but the average resistance would be greater than the cross-section, and it might be modified greatly by having a large number of holes which would take up fifty per cent. of the whole area. There is probably an effect due to same, but that other factor must be considered.

Mr. McElroy: I would say that the metal between the holes when figured up, and the length of the path when considered, does not account for the increase of the resistance. That has been carefully gone over.

Mr. F. A. Lidbury: Does that increase of resistance disappear when the metal is annealed?

Mr. McElroy: I have not discovered that that could be reduced by annealing.

Prof. W. D. Bancroft: The President has referred to the electromotive force as being the cause of corrosion. It is a cause, but it does not determine the whole behavior of the metal, provided you are dealing with anything more than infinitesimal corrosion. The other factor is whether a surface film has formed. You can compare a bar of zinc and a bar of iron. There is a greater potential difference between zinc and solution than between iron and solution. Zinc corrodes only to a slight extent, aluminum still less, and then the corrosion stops. Iron goes on rusting indefinitely under most circumstances. It is important to keep in mind that the only thing which the measurement of

electromotive force gives you is the first initial tendency to corrosion, and does not show in the least that the metal will actually corrode, using corrosion in the ordinary sense of the word.

Dr. Clayton H. Sharp: I would like to inquire whether anything is known as to the reason why deflocculated graphite acts as a protector of an iron surface, whether it is because it covers the iron with a coating of material which itself will not go into solution, which carries the current from the iron to the electrolyte as an intermediate metallic conductor between the iron and the electrolyte, or whether there is something else to account for its action.

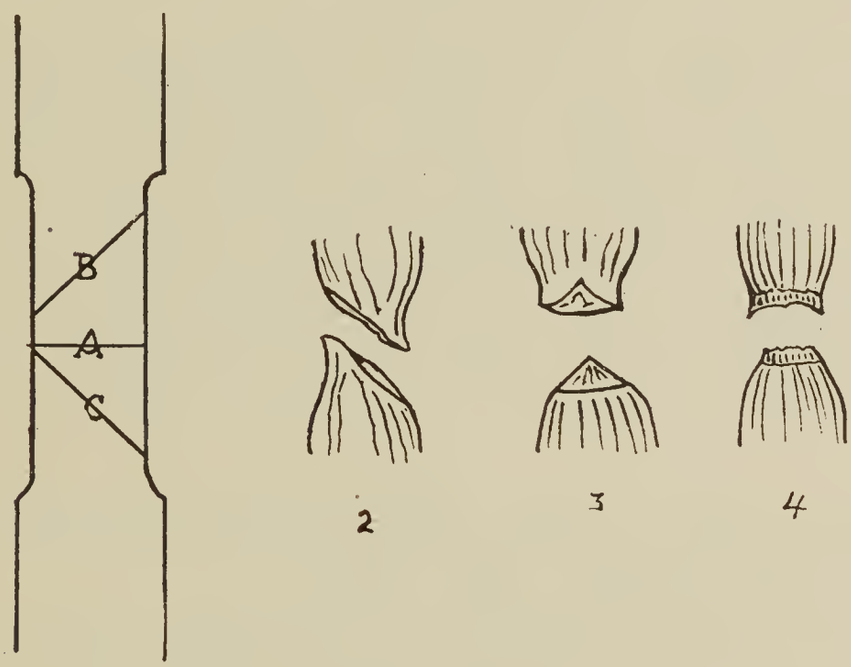

Fig. 1.

I should like to know if there is any possibility of the application of this method of protecting iron to protecting underground pipes, and so forth.

Mr. George G. Grower: There has been no reference made to thermo-electricity; it seems to me that part of the current observed might be of thermo-electric origin, iron ranking very high among metals in this respect.

On several of the slides shown the lines of corrosion are very marked, the speaker does not appear to be quite sure that these are lines of strain. I do not think there is much doubt about it. It might be interesting to refer to the lines of strain produced in breaking a sample of metal in a testing machine. In Fig. 1,

representing the usual shape of the test-piece which is being pulled apart, it would at first appear as though the lines of strain would be at right angles to the axis, as at A, but in reality they are diagonal as at B or C. These lines can sometimes be seen forming on the sample under test, and they generally begin at the shoulders and work toward the center. When the sample breaks it will not break straight across but at an angle as in Fig. 2, or a double angle forming a cone as in Fig 3; frequently the cone is truncated forming what is called a cup as in Fig. 4. Almost invariably samples will break in one of these forms, or a combination of them, showing that the lines of strain are in two directions crossing each other at an angle.

Mr. Carl Hering: I have been greatly interested in this paper which I think is one of the most instructive papers which has been presented to this Society. Professor Burgess referred to a case in which the iron was corroded when it was a cathode. I would be very much interested if he would say something further about it, as it seems to me that this is very important; we usually assume that the iron is free from danger of corrosion when the current enters it. If this is not true we ought to know it.

Prof. H. S. Carhart: I suppose the extent to which the electrolytic corrosion of iron takes place is undoubtedly understood by all the members of this Society.

But this is a very noticeable fact—if you have examined water pipes that have been corroded electrolytically, you must have noticed a scale on the pipes which you can cut off readily with a knife, consisting almost entirely of graphite or oxide; you will find it in spots, or in holes, so you can take a knife and by twisting it run it through the pipe. The metallic iron has disappeared. I think corrosion in water pipes generally takes place that way. These facts support what Professor Burgess has said, that the action in part, at least, may be voltaic action. We can see that in cast iron the graphite would be left there, if the iron is taken out, of course, but it is difficult to see why the corrosion takes place in spots in this way, unless there is more graphite in certain places than in others. Of course, the iron is not homogeneous, and the corrosion set up at any point would naturally continue there until the greatest damage is done.

I recently examined a water pipe which had been down only a little over two years, and which showed a marked amount of scale on the outside. I must confess that this occurred at a point where the street railway has been accustomed, at a crossing, to put salt on the street for the purpose of removing ice; and the earth is probably saturated with salt water, and that increases the corrosion. It may not be known the extent to which vertical pipes or rods or columns in the earth are injured by electrolytic action. I know a case where an iron pipe is down in the ground to a very considerable depth, and in a period of a few years there has been so much corrosion that the pipe has been eaten through, so that holes developed in it, and the pipe could not be employed for the purpose for which it was put down.

Another point occurred to me, and that is that this appreciable electromotive force, which Professor Burgess describes as having been obtained between strained and unstrained iron, may be explained, I think. Perhaps Professor Burgess has not had his attention called to the thermo-electromotive force, which is a source of electromotive force in addition to the energy of the strained iron. Say we had two sources of electromotive force (Professor Cahart then drew the Helmholtz equation on the board).

The thing which has been talked about is this first term, which may be heat of reaction, heat of hydration, heat of solution, heat stored as potential energy, due to the twisting of the spring, etc.; or it may be a variety of other things, small quantities of energy stored in the material. The second term is thermo-electric, because it is proportioned to the absolute temperature; that is evidence enough. In this case it is electrolytic thermo-electromotive force, as in a concentration cell, which is different from ordinary thermo-electromotive force between metals. Unless the experiment has been tried, of course, I have no evidence as to the direction of it, whether positive or negative in the case of the stretched iron. I have no doubt there is an electrolytic thermo-electromotive force there. If it is positive, the two terms can be added together and we get an electromotive force higher than the one calculated from the potential energy alone.

Another point is, in this case of the steam boiler, the electromotive force rose with the temperature. It would enter here as

due to pure chemical action, but it may be due in part to this electrolytic thermo-electromotive force. We should take that into account and see whether it is there.

It seems to me these experiments show we have voltaic action or electrolytic action taking place, which corrodes the iron.

President Burgess: Professor T. W. Richards has written me a letter in which he makes a comment and suggests it be read as his discussion of this matter. He says: "As far as my experience goes, electrodes which are not in equilibrium do not give constant results. Referring to the use of the ferric chloride, which is criticised, I have tried several other cases lower down, for example, in the hope that the kind of metastable form might be obtained, but without success. I should be interested to hear by what device you can give iron satisfactory results in ferric chloride, for of course, there must be some condition or circumstance which determines the difference between our experience."

In regard to Mr. Hering's question as to how current flowing toward the cathode will produce corrosion, I will say it does not, but sometimes it does, depending on conditions, but it will take too much time to go into that. That will be a subject for a paper. I might say briefly, however, that if there is a film effect which Dr. Bancroft speaks of, a film effect which will stop the corrosion, then this film can be broken up, if you have current flowing toward that as a cathode. Taking the case of ——— that will not corrode, unless you make it in the form of a cathode, and it will corrode freely. That is present in marked degree in iron, especially when exposed to certain acids.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., April 30, 1908; President C. F. Burgess in the Chair.

ELECTROCHEMICAL CORROSION OF THE ROCHESTER STEEL CONDUIT.

By Richard H. Gaines.

The water supply for domestic uses at Rochester is obtained from the Hemlock Lake, about 29 miles south of the city. Tapped from the lake at an elevation of 386 feet above the city level, the water is carried by gravity to the storage and distributing reservoirs by two separate pipe systems locally known as Conduit I and Conduit II. These conduits were laid at a depth of a few feet, a short distance apart, and follow the natural undulations of the surface wherever the land lies below the hydraulic grade lines.

Conduit I.—The older of the two pipe systems, known as Conduit I, was constructed in 1873-4-5, and was laid as follows: The first section is about 10 miles long, extending northerly from the intake at Hemlock Lake, and consists of 36-inch wrought iron pipe with cast-iron hubs and spigots, and poured-lead joints. The next section proceeding north about one-third of a mile, is also of wrought iron, 24 inches in diameter, jointed in the same manner. The next section for a length of 5¾ miles, is 24-inch cast iron pipe, and this is succeeded by 2⅝ miles of 24-inch wrought iron pipe. The last 8¾ miles is again 24-inch cast iron pipe. The last section ends in Mt. Hope distributing reservoir, the conduit on the way connecting at Rush with a storage reservoir.

There is little to be said about the cast iron sections of this pipe. The important fact to be remembered is that no rust holes have appeared in this part of the conduit. During 32 years of service, leaks have occurred from time to time at lead joints, and tubercles forming on the interior have reduced the carrying capacity, but otherwise it has given no trouble.

The first two sections of Conduit I were constructed of riveted plates of wrought iron 4½ feet long and from 3/16 to ¼ inch in thickness. Prior to laying this pipe in the earth, it received a coating by the usual dipping process in an equal mixture of Trinidad asphalt and coal tar pitch.

Conduit I, as a whole, has given excellent service from the beginning. In 1894, Chief Engineer Kuichling stated that there had been but one leak from corrosion, and not one cent had been expended for repairs during the 19 years the pipe had been in operation. A few small leaks in the wrought iron section (less than 10 in number) were discovered at intervals and repaired between 1894 and 1904, but none have been reported since the latter year. According to recent reports from Rochester, Conduit I remains generally in good condition after more than 32 years' service. During this long interval the pipe has been under the constant surveillance of overseers and such trouble as supervened from corrosion has been of a trifling character.

It will be shown later that the soil in which this pipe was laid, and other circumstances surrounding it, were anything but favorable to its preservation. A better example could hardly be found of the durability of wrought iron under trying conditions.

Conduit II.—Fourteen years after Conduit I went into service it became evident that the supply of water furnished would be insufficient for the increasing population of Rochester. Investigations and reports by engineers led to the decision, in 1890, to lay a new main from Hemlock Lake to the city. Conduit II, which was subsequently built, contains apart from its magnitude many points of unusual interest worth relating.

About this time, 1888-90, the use of steel for large water pipes was beginning to be adopted. New methods had come in response to an urgent need in engineering construction for a metal which would be as soft as wrought iron, as strong as steel and cheaper than either. These advances had resulted in a cheap and abundant supply of mild steel, which was now rapidly displacing wrought iron. It was claimed that iron refined by the new processes was practically free from carbon and cinder, and combined all the best qualities of wrought iron with the added strength of steel. In this state it was thought to be especially adapted to the manufacture of water pipe, although

little was known of its durability. These statements are intended not so much to show how the use of steel pipe began, as to call attention to the very brief period that has elapsed since its advent—less than 20 years.

The East Jersey Water Company was one of the pioneers in the use of large steel pipe, letting a contract in 1890 for a 21-mile line of 48-inch, and a 5-mile line of 36-inch, riveted steel water supply conduit for Newark. Other water companies and several cities were contemplating the use of steel. No particular warning seems to have been given by the experts consulted of the danger or possibility of deterioration.

The foregoing facts, and particularly the relative cheapness of steel, led the authorities at Rochester to decide upon this material for the new main. The final contract was let in January, 1893. The conduit as completed two years later will be described in some detail. The data for the following description were collected during a recent visit to Rochester for a personal inspection of an uncovered portion of the conduit, from special reports of Chief Engineer Kuichling, published in the "Engineering News," and from reports of the Rochester Department of Public Works.

Excluding the intake pipe and the gate-house at the lake, this aqueduct consists of a brick conduit of horseshoe-shaped cross section, 6 feet high and wide inside, and 2½ miles long, terminating in an overflow chamber 34 feet long, the north end of which forms the beginning of a 38-inch pipe conduit about 26¼ miles in length, connecting with the Rush storage reservoir on the way, and ending at the Mount Hope distributing reservoir. About 26 miles of this length, is 38-inch (inside diameter) steel pipe, and ¼ mile, 36-inch cast iron pipe.

The main pipe conduit was constructed of soft open-hearth steel plates nearly 7 feet long and ¼ to ⅜ inch thick, riveted as cylindrical inside and outside courses, alternating, and forming a tight fit with each other before the protective coating was applied. Soft steel rivets of the same composition as the plates were used for riveting.

The specifications for all material used in the construction of this pipe were drawn with great care, and after exhaustive study by Emil Kuichling, Esq., C. E., the Chief Engineer in charge

of the work. The specifications called for soft open-hearth steel containing not over 0.6 per cent. manganese and 0.06 per cent. phosphorous, with a tensile strength of between 55,000 and 65,000 pounds, and an elastic limit of not less than 30,000 pounds. The thicknesses of the plates were manufactured and arranged according to the pressure to which they would be subjected in the line of the conduit. For pressures due to a static head of 120 feet or less, ¼ inch thickness was demanded; with a static head ranging from 120 to 200 feet, 5/16 inch; and for over 200 feet head, ⅜ inch. All plates less than 95 per cent. of the required thickness were rejected without appeal.

The steel pipe for the southern half of the conduit was supplied by the East Jersey Pipe Company, of Paterson, N. J., and that for the northern half by the Rochester Bridge & Iron Works. The steel plates used at Paterson were made by the Carnegie Steel Company, and those from the Rochester shops by the Paxton Rolling Mill, at Harrisburg. Before delivery from the mills the plates were inspected and approved by Booth, Garret & Blair, the well known metallurgical chemists.

The Methods of Coating.—Numerous experiments with different kinds of asphalt and other substances were made under the direction of the engineer in charge during the years immediately preceding the construction of the conduit. All the materials, however, that were subjected to a practical test gave more or less unsatisfactory results.

After the decision was reached to use steel in the new work, the best experts were consulted concerning the question of coatings. Prof. A. H. Sabin, of New York, was engaged to conduct a series of investigations, with the hope of developing a method that would be both practical and permanent. Before Prof. Sabin's experiments were completed the work had to be proceeded with.

The first section of the pipe, 7½ miles in length, nearest the lake, was given a coating of California asphalt by the East Jersey Pipe Company, similar to that applied to the large steel conduit just completed for the water supply of Newark, N. J. The method used in applying the coating was as follows: After a pipe was riveted and calked it was thoroughly cleaned, heated in an oven to about 300° F., and then dipped horizontally in a

large tank containing the hot coating material (kept at an average temperature around 350° F.) where it was allowed to remain for such time as would suffice for the temperature of the metal to become the same as that of the mixture. The pipe was then removed from the bath, the surplus coating allowed to drip off, and it was then placed on skids outside, where the material was left to harden.

The results at first appeared to be satisfactory, but after the pipes had been exposed to the air for several weeks the high gloss gradually disappeared, leading to the inference that the substance was undergoing a slow change. In fact, the coating showed signs of disintegration before the pipe was put into the trenches. Moreover, it failed in adhering tightly to the metal, and the contractors were subjected to much expense in painting over many spots and larger areas from which the coating had scaled off during the transportation and handling.

For the next 5½-mile section of the conduit directions were given the East Jersey Pipe Company to substitute for the California asphalt a mixture of refined Trinidad asphalt and the best grade of coal tar pitch in equal proportions, thereby producing the same coating as had been applied to the old conduit, and which in that case had apparently proved durable. Although this mixture was more satisfactory on the whole than the California asphalt, it left much to be desired in toughness and adhesion to the steel. The East Jersey Pipe Company had now about completed their portion of the work.

Meanwhile, promising results obtained by Prof. Sabin from experiments with a japanning process led to the adoption of this method for the northern half of the pipe. The Rochester Bridge & Iron Company applied the process under the supervision of Prof. Sabin at a plant especially provided near the shops. Sections of the pipe 27⅓ feet long were first heated in an oven to a temperature of 300° F., then dipped vertically in the hot coating mixture at the same temperature. Upon removal from the bath, the pipe was allowed to drain and then transferred to a large brick oven, kept at a fairly even temperature of about 500° F., where it remained 10 hours, after which it was ready for use. The materials were all prepared on the spot; their precise composition was not stated. Baked japans, however, are usually

made from linseed oil, and asphalt as a base, mixed with more or less copal resins, and are thinned with turpentine. The preliminary heating of the pipe before immersion in the dip assures its adhesion and impermeability. Although more expensive than the other methods, it was claimed that the japan coating was elastic, impervious to atmospheric influences, running water, dilute acids or alkalies, and owing to the nature of the ingredients electrically passive, except to currents of high voltage.

After the conduit was completed the chief engineer expressed great satisfaction with the japan coating, stating that it was superior in all respects to those which were applied to the southern half of the pipe. For a time it was generally considered that baked japan coatings left but little if any room for improvement in the coating of water mains.

Shortly after the completion of the work, and years before any trouble developed, the chief engineer, in a report, expressed apprehension about the southern half of the conduit, stating that the coating used to protect the pipe there had failed to adhere tightly to the metal. Moreover, it was said that in spite of all precautions there were numerous abrasions both during transportation and in the field, *i. e.*, while getting the sections of the pipe riveted together in the trenches. A preparation called "P. and B. Paint" was selected for repairing the bare spots, which was applied with a brush to the cold pipe in the field. The defects of this remedy, and the material, will be referred to later.

Abrasions in the Sabin coating were repaired with an air-drying varnish, similar in composition to the japan mixture used at the shops.

General Data.—The pipe was generally furnished in sections 27⅛ feet in length, consisting of four courses riveted together in the shops, and having all seams thoroughly calked both inside and outside. After the pipes had been coated and delivered along the route of the conduit, two lengths were riveted together upon the surface of the ground, thus forming a section about 54.5 feet in length. These sections were then rolled in succession by a large number of men upon suitable timbers laid across the trench, from where they were lowered into position by derricks.

It was contemplated that the pipe conduit should be a con-

tinuous, riveted tube throughout its entire length, without expansion joints or other mechanical devices for compensating changes in length caused by variations in temperature. By this continuity such changes are prevented from manifesting themselves and are replaced by internal stresses in the metal, which are far within its elastic limit for the range of temperature encountered in the work. Motion was prevented by bedding the ends of the pipe in large masses of masonry.

As stated at the outset, the steel conduit goes through the same territory as Conduit I, the distance apart varying from 25 feet to an extreme of about 1 mile. It is therefore subject to practically the same external physical conditions. The greater portion of Conduit II is laid through fine farming country and, as in the case of Conduit I, this pipe conforms to the general undulations of the land through which it passes.

Conduit II went into service as soon as completed in 1894. During the succeeding years it was thoroughly inspected outside every summer, and once or twice examined inside. From 1894 to 1900 a few insignificant leaks due to imperfect calking were found. In a 200-foot section of the interior of the northern portion a negligible quantity of tuberculation was all that was seen. To all appearances the conduit had remained in good condition during the first 6 years after its completion.

Rust Leaks.—In 1900 two small leaks were discovered near the southern end in the part of the pipe coated with California asphalt, which were caused by corrosion of the steel plates. In 1901 thirteen rust leaks occurred in this part of the conduit, three of which were in a single plate. At this point the pipe was uncovered for a short distance north and south, when several plates were discovered that were badly corroded and the coating in poor condition. Numerous pits were found in the steel varying in size from ⅛ inch to 1 inch across, and in some cases ⅛ inch deep. It was easy to see that if let alone, these pits would in time develop into rust holes.

At first the corrosion seemed to be more or less confined to about 2,000 feet of Section 1 of the southern division of the conduit, and was believed to be due to some local conditions. The reason first assigned was that the pipe plates there were probably of poorer quality than on the rest of the line. But later, as the

trouble began to spread, it was deemed advisable to begin a careful investigation of all sections of the conduit. Test holes were dug, and trenches of several hundred feet were excavated here and there all along the line of the pipe. Throughout the southern half of the conduit where asphalt and coal tar pitch had been used, the coating was found to be in poor condition, and many plates were pitted. Wherever the pipe was found to be corroded it was scraped, painted and occasional leaks were repaired.

The inside of the conduit was also examined near the south end of the line for a distance of 250 feet. Considerable tuberculation was found, some sheets having as many as 100 tubercles, on the removal of which pits were revealed. No leaks, however, have been observed as coming through from pits on the interior of the pipe. Repairs to the pipe were made by closing the hole with a wooden plug, then recovering it with a patch of sheet lead, and a steel patch, held in place by heavy iron bands or clamps passing around the pipe, after which the outside edges of the lead were calked.

The reports contain no reference to corrosion in the northern half of the conduit until 1903, when four rust leaks appeared in a small section of pipe laid through a swampy area. At the end of 1906, only fourteen leaks in all had been discovered in the half of the conduit coated by the Sabin japan process, and these occurred in a section of the pipe less than ⅔ of a mile in length, in wet, low ground, mainly a cedar swamp.

Since the trouble made its appearance in 1900, the whole line of the conduit has been under the rigid scrutiny of overseers stationed on the different sections.

The following table gives a list of leaks caused by corrosion in the steel pipe, with the divisions and years in which they occurred.

Year.	Rust Holes.	Section.
1900	2	I.
1901	13	I.
1902	5	I.
1903	18	4 in Section I. 8 " " II. 6 " " III.
1904	38	19 in Section I. 19 " " II. 0 " " III.

Year.	Rust Holes.	Section.
1905	34	25 in Section I. 6 " " II. 3 " " III.
1906	33	20 in Section I. 8 " " II. 5 " " III.
1907 incomplete	21	
Total number of leaks	164	

Section I coated with California asphalt.
Section II coated with Trinidad asphalt and coal tar pitch.
Section III received the Sabin japan coating.

Method of Combatting the Corrosion.—As soon as the full gravity of the trouble was realized, steps were taken to arrest or prevent further damage by recoating the pipe. The work has been chiefly done during the summer months each year, the following method being pursued: Wherever the pitting or corrosion is active the pipe is uncovered in short sections and scraped clean. The pits are thoroughly cleaned out with a sharp instrument and afterwards heated sufficiently with a blow-lamp to dehydrate any rust left. As soon as the pipe has been made ready in this way it is given several successive coatings of waterproof paint applied with a brush; first a coat of Superior Graphite Paint No. 501, which is allowed to dry; then a coat of Superior Graphite Paint No. 106, which is allowed to dry; two coats of Mineral Rubber Paint G. B. are then applied at short intervals, and as soon as the paint is dry the trench is refilled. Canvas awnings are provided to protect the exposed pipe from the weather. The portions of the conduit affected by corrosion will continue to be recoated in this manner as rapidly as practical, thus anticipating leaks in many cases and providing better protection to the metal in the danger districts.

The method of repairing the smaller leaks has been previously described. When, however, the patch has to cover a considerable area due to a series of holes or pitted places which are so continuous as to preclude the use of individual small patches, or where the plate is so weakened as to need a continuous cover plate of considerable size, an elastic cement sold under the trade name of "PYROCENIT" and manufactured at Paterson, N. J., has been successfully used. This material is furnished in two parts, a

powder and a liquid, which are intimately mixed to form a stiff paste. It expands slightly on setting, is water-tight and adheres closely to the metal which it is also said to preserve.

Observations at Rochester.—While the work of recoating the pipe was in progress during the past summer, and in response to an opportunity afforded through the courtesy of City Engineer Edwin A. Fisher, the writer was directed to accompany T. C Atwood, Esq., assistant engineer, to Rochester for an examination of an uncovered portion of Conduit II, where a typical case of corrosion might be seen. On the 14th of June, with the co-operation of John F. Skinner, Esq., principal assistant engineer in charge, we were shown in an open meadow, two miles southeast of Honeyoe Falls and about 10 miles north of the Hemlock Lake, an exposed section of the pipe several hundred feet in length. The conditions existing in this section were supposed to be fairly representative of the un-recoated portion of the southern half of the conduit. The writer got into the trench and examined the pipe with care for more than 300 feet. On close inspection it was found that about 4/5 of the plates were still in good condition. In the remaining ⅕, however, the destructive process of corrosion was active, and the effect was very apparent. In many of the plates the corrosion was in its initial stages, while in others it was far advanced with multiple pits, and the occasional ominous evidence of a perforation that had been repaired with a patch in the manner previously described.

The Corrosion Centers.—The "pittings" or rust deposits were small raised surfaces nearly circular in shape, although some of them had an elongated, irregular outline. The soft rust at these spots could be readily cut away with a knife. Wherever the rust was all taken out, a clean, round hole with characteristic sharp edges would be found, from ⅛ inch to ⅞ inch in diameter, and 1/16 inch to ¼ inch deep. The holes looked as though the metal had been drilled out with a sharp instrument. Some of the plates presented the appearance of having been pock pitted, or attacked by a corroding disease.

Inside the Pipe.—No opportunity was presented of seeing the condition of the interior of the pipe at this time. The engineer

in charge, who had made previous examinations, reported numerous tubercles on the inside of the pipe which covered pits shaped in cross-section like the cross-section of a saucer; the outside pits were more like the cross-section of a cup. The inside corrosion does not appear to be of a serious nature in any event. Whereas 164 leaks have occurred due to outside corrosion, not one has yet been discovered as proceeding from the inside. This last is probably due to the fact that on the inside of the pipe there is a constant current of water flowing, and the electrical conditions there are uniform. Iron or steel exposed intermittently to the action of water corrodes much faster than when immersed in water all the time.

The Condition of the Coating.—The uncovered portion of the pipe examined on the 14th of June had received as a protective coating nearly 14 years previously, a mixture of Trinidad asphalt and coal-tar pitch. The condition in which the coating was found varied in different sections according to the thickness of the original covering, and the amount of water in the surrounding soil. Many surfaces were found (especially in springy or wet areas) on which oxidation and decay had finished their changes, and the coating had completely lost its efficiency. Other sections of the pipe, laid in the soil that was more porous and that had probably retained a thicker covering after leaving the vats, had undergone considerable change, yet the process of oxidation had not destroyed the coating. These irregularities can be ascribed not only to inherent defects in the material itself, but to the sheer impossibility of securing anything approaching a uniform thickness of coating on the metal by the method used for its application.

Study of the Causes of Corrosion.—When the trouble first appeared it was supposed to be possibly due to "stray" currents, although no car lines or other artificial sources of electricity were near. The electrician in charge of the municipal laboratory at Rochester made a careful survey along the whole line of the conduit. No measurable current could be found with the millivoltmeter from outside sources, even where the pittings were worst. All the galvanometric readings thus made gave negative results. The explanation was therefore to be sought elsewhere.

As a preliminary step in the studies to ascertain the cause of

corrosion in the steel conduit, the writer collected samples of soil, drain water, steel, rust from the pittings and samples of the coating for examination or analysis at the laboratory.

The Soil.—The underlying rocks of the particular area visited were observed to be shales, with some limestone outcropping here and there. The lands generally throughout the district are upland meadows and apparently fertile. No unusual conditions occur other than ordinarily seen in open country, miles away from town or village. The soil surrounding the pipe where uncovered was quite uniform in character—a heavy clay, usually light in color, rarely red, and almost saturated with water wherever the pitting was worst. No evidence was observed of any special local corrosive influences, such as gases in the earth, acidic rocks, or their decomposition products.

A complete analysis was made of the sample of the soil taken from the trench, within a few inches of a badly corroded section of the pipe, with the following result:

Silica, SiO_2	50.42
Alumina, Al_2O_3	15.65
Lime, CaO	12.36
Magnesia, MgO	3.64
Iron Oxide, Fe_2O_3	1.71
Manganese Oxide, MnO	0.55
Potassium Oxide, K_2O	1.04
Sodium Oxide, Ma_2O	0.47
Sulphur Trioxide, SO_3	0.35
Loss on ignition (chiefly water of hydration)	14.13
	100.32

No unusual ingredient was revealed in the soil by this analysis. The water extract from an infusion of a portion of the sample gave a neutral reaction with the most delicate tests, indicating the absence of any abnormal acidity or alkalinity.

The mere chemical composition of a soil will not always indicate its corrosive character, although necessary to be determined, because the earth from local causes may be impregnated with substances almost unknown in the pure soil. The chief value of chemical analysis is in detecting the presence of certain soluble salts which, if present, are decidedly corrosive. Especially is this true of the chlorides of the alkalies or alkaline earth metals

which induce chemical action catalytically, and moreover afford a ready medium for electrolytic conductivity.

Extraction by infusion with distilled water of several samples of soil collected from the trench, in close proximity to corroded plates, gave an average of about one per cent. of soluble material. The salts thus dissolved were found on qualitative analysis to consist chiefly of sulphates and chlorides of lime, magnesia, soda and potash. The part played by these strong electrolytes in the corrosion of the pipe will be referred to later.

Ground Water.—Samples of water were collected from under the pipe where corrosion was active, and also from a surface drain near by. These samples were found to contain an unusual quantity of both chlorine and free carbonic acid. The presence of certain organic matter, however, as well as phosphates, indicated human contamination, and thus no useful deduction could be made from the analyses.

Composition of the Steel.—The specifications for the Rochester conduit as stated previously, called for a soft, low carbon steel. Two samples of this steel were procured through the assistance of John F. Skinner, Esq., which gave the following results on analysis:

	No. 1. Drilled from Unused Plate. Per Cent.	No. 2. Clippings from Pipe. Per Cent.
Total Carbon	0.13	0.15
Silicon	0.13	0.10
Manganese	0.34	0.36
Sulphur	0.04	0.05
Phosphorus	0.011	0.009

The feature of these results is the low content of impurities. It is difficult to see how much segregation could take place in a steel so good as that shown by the analyses.

The Rust.—An average sample collected from a number of the pittings or rust deposits was analysed with the following results:

		Per cent.
Metallic Iron	Ferric	31.17
	Ferrous	4.55
Carbon (by combustion)		0.27
Carbon Dioxide		2.88
Water	Hydration	17.02
	Moisture	22.80

From which the following composition was calculated:

Ferrous Carbonate, $FeCO_3$	5.56
Ferrous Oxide, FeO	2.40
*Other Iron Oxides and Hydrates	68.97
Carbon	0.27
Moisture	22.80
	100.00

Several samples of the rust were carefully examined both macroscopically and microscopically for any inclosed particles that might have been the cause of local action. The results, however, were negative. Qualitative analyses were also made of other samples of rust cut out of pits in the pipe, but nothing could be detected besides hydrated oxides of iron, a small amount of ferrous carbonate and a trace of organic matter.

The Coating.—A sample of the coating in its semi-oxidized state was scraped from the pipe for examination. This specimen gave on analysis:

Bitumen .....65.21 per cent.

An effort was made to determine if the decomposition products of the coating were corrosive in action on the pipe. Several samples were collected near corroded spots, and afterwards extracted with warm distilled water at the laboratory. The extracts gave a neutral reaction, proving that none of the trouble had proceeded from this source.

The Results of the Examinations.—The cause of corrosion in the steel conduit cannot be accounted for by any single circumstance. The survey for outside currents ("stray currents"), the character of the soil, the water draining away from near the pipe, the composition of the steel, the contents of the rust deposits, the coating and its decomposition products—none of these sources when studied singly offered a satisfactory explanation for the trouble. After a careful survey of every factor that may have played any part, either singly or combined, the conclusion was reached that the corrosion resulted rather from a combination of physical conditions than from causes that were chemical. Immediately

* There is no definite hydrate of iron of the form $Fe_2O_3 + H_2O$. The ratio of Fe_2O_3 to H_2O is a variable one and may be anything according to circumstances. The normal hydrates are derived from the oxidation of ferrous salts.

after examining the steel pipe, the writer made this note: "On the spot it looks as though the damage is due to defects in the coating, and minute physical irregularities in the plates." If to these two causes be added water-logged soils in contact with the pipe, the explanation of the trouble is at hand.

The portion of the steel pipe examined was laid in the earth at a depth of from 4 to 5 feet, a stratum in which a large amount of water is held by capillary attraction. This maximum water table, as it is called, is below the influence of surface evaporation in the clay soils, and above the influence of underground flow. The ground water in these places, from its long contact with the earth, becomes laden with soluble salts. Thus a blanket of wet soil holds a jacket of electrolytes about the pipe, giving rise to all the conditions necessary for active corrosion, wherever the coating may have given away by abrasion or otherwise. The imperfect protection afforded by the coatings is self-evident, since corrosion could only occur where the metal was exposed to moisture or corrosive solutions. Inadequate protection must be admitted, therefore, as a prime cause. This of itself, however, is insufficient to account for the trouble, since plates were examined on which the coating had long since disintegrated, and no evidence of corrosion was apparent.

That soil influences played a leading part in the corrosion is obvious, from the fact that the damage to the pipe was confined to ground conditions of a definite character, *i. e.*, soils in which was normally present an excessive amount of water. The number of plates not visibly affected in the wet areas, however, proves that the trouble cannot be ascribed to the soil alone.

It is certain that local irregularities in the steel was a factor in the corrosion, because where subjected to precisely the same influences in the moist areas, some of the plates were corroded and many were not. But the corrosion cannot be wholly charged to local irregularities of structure and composition in the corroded plates, for whenever the soils were of a porous or sandy nature, permitting excess of water to evaporate or sink unimpeded into the earth the trouble does not occur at all.

The conclusion, therefore, follows that damage by corrosion in the steel conduit where three conditions meet and co-exist:

Ineffectual coatings, (normally) wet soils, irregularities of

structure and composition of steel. These three influences in combination resulted in auto-electrolysis—a word proposed by the writer for intense local action as manifested by "pitting," in the absence of outside currents of electricity.

Since the causes of serious damage to the Rochester Conduit may, with slight modifications, exist anywhere, the conditions which led to trouble there will be discussed in a somewhat general manner.

Defects of Bitumen Coatings.—Under the trying conditions described, such coatings as were used for the southern half of the conduit (California asphalt and coal-tar pitch) afford protection to water pipe for only a brief period at best. It was inevitable that trouble would occur in the wet soils of the areas through which the pipe was laid. Official reports of the work at the time, stated that much trouble was encountered with the asphalt coatings, which failed to adhere tightly to the metal, and besides numerous small abrasions were unavoidable. Some of this trouble was no doubt due to the imperfect contact between the coating and steel. Apart from the fact that the melted bitumens are by nature electrically negative, the dense film of air which normally covers the surface and penetrates the mass of metals, is exceedingly difficult to remove, and thus, indeed, it is doubtful whether anything more than partial contact ever takes place between bitumen pipe dips and steel under the conditions. There is no coherence or chemical bond between the two, and over considerable surfaces the coating is but loosely held in place by mechanical adhesion, a very different force from the mutual attraction which particles of the same body exert on one another. The space that separates the two may be less than $\frac{1}{10,000}$ of a millimeter, yet if the distance is beyond molecular range, it is sufficient to explain why the coatings do not continue to remain attached to the steel under shocks or strains, or severe atmospheric conditions.

A better protection would be afforded were it not for the lack of mobility, or the viscous resistance of the asphalt, which cannot enter and fill the pores of the metal on account of the high surface tension. Another inherent defect is that the asphalts are partially volatile at the temperature the pipe is dipped, giving off vapor continuously. An evidence of this is the vapor films,

and bubbles which may be seen in a coated specimen under the microscope, and which are no doubt sources of weakness. Owing to the volatile hydrocarbons present, it is next to impossible to keep the melted pipe-dip in a uniform state of mobility. So-called fluxes are poured into the vat from time to time, to prevent the materials from becoming too immobile, but this remedy gives unsatisfactory results in practice, the melted liquid constantly varying in viscosity.

Perhaps the most serious imperfection connected with these coatings arises from the method of application. The pipe is heated to about 300° F., and then lowered either vertically or horizontally into a vat of melted pipe-dip ranging in temperature from about twenty degrees below to twenty degrees above 350° F. When slowly removed the pipe is held in an inclined position above the vat until the excess coating drains away. Consequently the coating may be from ¼ to ⅜ inch thick at the lower end, and less than 1/32 inch at the upper, when the pipe is rolled out on the skids. Wherever the coating is of slight or inadequate thickness it is easily ruptured by strains and soon breaks down on exposure to adverse conditions.

The regulation of the temperature of the vat during the dipping process has apparently received insufficient attention. After the best dipping temperature has been ascertained by experiment, the range of temperature of the liquid bitumen should be kept at a minimum, or as nearly constant as possible. An important fact that seems to have been overlooked in practice is that the properties of the asphaltic compounds, like other amorphous bodies, undergo a steady change with rise of temperature. A difference of thirty or forty degrees may cause a decided difference in the character of these substances.

It is unknown to what extent bituminous pipe-dips, as now applied, hold in check corrosive influences in the soil. Unfortunately, the published data relating to the subject must be taken *cum grano salis,* since it has chiefly emanated from corporations engaged in exploiting some particular asphalt or other bituminous compound. It has been proved time and again that bitumen coatings will not prevent the corrosion of underground steel pipe where the soil conditions are really severe, *i. e.,* if chlorides, acids, electric currents, or any of the energetic rust formers are present,

along with excessive moisture. "Pittings" have been found in steel plates where the coating was apparently in a fair state of preservation, which demonstrates that the coating was neither proof against moisture nor the passage of currents from the pipe into the ground, causing electrolysis.

A high (United States) government authority, after years of study and observation of these materials, recently told the writer that he had come to look upon all bituminous coatings as mere makeshifts and of doubtful advantage. This view may be regarded as extreme, yet from the nature of the materials there is reason to believe that this cheap method of coating cannot inhibit corrosion long. After application, the bituminous compounds undergo progressive molecular changes, lose elastic quality, become brittle, and owing to the high expansion coefficient of steel, in time form a network of cracks through which moisture attacks the metal. Laboratory tests with small coated specimens kept in contact with water in glass jars proved that some of the asphaltic compounds break down and disintegrate in a few months. Trinidad asphalt especially was shown to be quickly attacked by water, and it is no longer used for waterproofing. The tests demonstrated that there was considerable difference in the durability of the products, but no chemical method has so far been devised for recognizing the inferior materials. Some of the compounds are manufactured from "blown oil," to which has been mixed a variable quantity of refined bitumen. The usual chemical and physical analyses do not reveal this fact, however, nor do they afford any reliable means of judging of the relative value of the different brands. Practical tests alone can determine their durability.

The Method of Repairing the Coatings.—The breaks in the coatings or abraded spots on the steel pipe were recoated with P. and B. Paint, a material which is prepared by dissolving a mixture of California residual pitch and maltha in carbon disulphide. When spread upon a cold surface the volatile ingredient which gives this paint flexibility is absorbed by air and water. The earthy constituent alone is left, and this being without coherence, falls off, leaving the spot bare as before. Every such surface readily becomes the center of chemical and electrical

activity when in contact with soil water, as manifested by corrosion.

Corrosive Influence of Soils and Water.—The portion of the steel conduit examined was subject to severe corrosive influences on account of the physical and chemical character of the soil. The conditions observed were reported to be fairly typical of the areas wherever the trouble had occurred in the southern half of the conduit. That the soil played an important role in the corrosion is proved by the fact that the trouble only occurred to a serious extent in wet clay or water-logged soils, *i. e.*, ground conditions in which excessive moisture was the normal state. As will be shown later, because of the remarkable power of dissociating the molecules of other substances, water readily becomes the medium by which the earth conducts electrolytically, and is therefore the arch enemy from which underground steel pipe should be shielded. The only possible solution of the corrosion problem lies in the prevention of the access of water to the surface of such structures.

Under all conditions, water is the essential agent of deterioration or decay in buried metallic structures; other influences, electric currents, atmospheric air, chlorides, organic and inorganic acids, promote or accelerate the process when acting with or through the medium of water, but would be inert in its absence. Owing to the mobility of its ions, water is not only the main vehicle for the processes of life, but also the principal medium of the changes that take place after death. The chemical and electrochemical reactions that occur in the animal, vegetable and mineral kingdoms are hindered or stop altogether in the absence of water. As found in nature, water is never pure, and the intensity of its corrosive nature can be gauged by the character and concentration of the gases and salts held in solution. The air contains innumerable solid particles consisting of organic matter, common salt, sulphate of soda, lime salts and other electrolytes, including corrosive gases, all of which are brought down by rain. After reaching the earth the composition of the water will be affected by the character of the surface soils and subsoils it flows over or sinks through. Waters flowing over rocky or clean beds of gravel and sand are obviously much purer and less corrosive than when contaminated by cultivated land where there

are deposits of animal or vegetable matter undergoing decay or putrefaction.

Touching the chemical nature of the soils in contact with corroded portions of the Rochester Steel Conduit, analysis revealed the presence of minute amounts of certain soluble salts (chlorides), which are among the most energetic and formidable rust formers of nature. These substances have the power of overcoming "passive" resistance catalytically, or by chemical induction, and thus render metallic surfaces "active," *i. e.,* subject to corrosion, by giving the preliminary impulse needed to dissipate chemical equilibrium. Passive resistance belongs to a class of phenomena of which we have little definite knowledge. A characteristic of the passive state is that it prevents the mode of motion incident to chemical change. Incidentally, it might be said that if some means could be discovered of rendering metallic surfaces permanently passive, the corrosion problem would be solved. Frequent attempts to devise such a method have hitherto been unsuccessful.

Corrosion is primarily a solution process, oxidation being due to secondary reactions. Since water is the universal solvent of nature, it is the principal medium of the corrosive changes that take place in buried metallic structures, and the rate of deterioration will generally vary according to the porosity or imperviousness of the soil. Soils absorb water or allow it to percolate. Apart from porosity, the amount of percolation is governed rather by the time at which the rain falls and the manner in which it is distributed than the actual quantity. The density, looseness, or open nature of the soil much affect absorption. Thus, loam, sandy and gravelly soils readily admit water, but on account of their incoherent quality offer slight resistance to its passage into the greater depths of the earth. The water of the soil does not entirely get beyond atmospheric influences, even at a depth of ten feet; thus, sandy, porous and gravelly soils lose much of their water by evaporation, while clay soils absorb water like a sponge, and hold it tenaciously. From the accumulation of water in relatively impervious strata of this latter character the soil becomes water-logged. Such clayey or marshy grounds are generally actively corrosive, and steel pipes buried in soils of this nature are in the perpetual state of siege. Precisely these condi-

tions were observed around the damaged sections of the uncovered steel conduit at Rochester. No coating has yet been found that would permanently withstand severely corrosive influences of this character. Under the circumstances described, it was shown that asphaltic pipe-dips are mere expedients, which may delay, but do not prevent corrosion.

In porous, gravelly soils, the corrosion processes are either inactive or proceed very slowly, even in the absence of protective coatings. Moreover, the oxidation changes suffered by the usual coatings are greatly retarded.

No serious trouble has occurred in the portion of the steel conduit where the soil conditions are like those last described.

Irregularities of Structure and Segregation.—Although defective coatings and soil conditions determine the extent of rust formation in underground steel water mains, the character of the corrosion is fixed by physical irregularities or segregation of impurities in the metal. The fact that some of the plates of the Rochester steel conduit were damaged by pitting, and a greater number were not, where the influences were identical, proves conclusively that some inherent property in the metal was a factor in the trouble. Unless irregularities of structure or composition exist, there can be no difference of potential, and thus the corrosion would not be localized or concentrated at definite foci.

It is probable that surface irregularities in the pipe conduit were physical rather than chemical, as it is unlikely that much segregation could take place in steel as good as that shown by the analyses. Influences, apparently slight and of no account, utterly change the structure and physical properties of steel, while not affecting the composition. For example there are certain critical temperatures, around which important molecular changes occur in steel. If a specimen of mild steel, containing 0.35% carbon be heated for two hours at 675° C. and cooled slowly, and another piece of the same steel be heated two hours at 775° C. and cooled in air, and prepared sections of each are afterwards examined under a microscope, the two will present a very marked difference of crystal form. Such modifications of structure cause variations in the solution pressure in different portions of the same plate, and give rise to sufficient difference of potential to

start localized corrosion processes in wet soil or in the presence of other suitable media.

In general, iron which has been subjected to a strain or uneven treatment corrodes much more readily than that which has been treated uniformly. The strained part becomes electropositive to the unstrained. It is well known that mechanical stress, scratches, or what Dr. Cushman has called wounds to steel, render the portion affected doubly susceptible to corrosion. Moreover, accidental breaks, either in the surface of the metal or the scale, have an important influence in locating corrosion centers.

With reference to local irregularities of structure, it is a physical impossibility, even with the most refined methods, to treat all steel surfaces, or the whole of any steel plate, alike. Besides blows, strains and other causes of local surface differences, the center will cool more slowly than the edges, and this cannot be prevented.

On account of the minute percentage of impurities contained in the low carbon steel of the Rochester conduit, it is not probable that segregation played any serious part in the trouble there. Since this inherent source of corrosion, however, is never entirely absent from steel, salient facts concerning it will be given. Segregation is the collection in spots by molecular action of metalliferous matter, differing more or less in texture and composition from the material in which it is enclosed. Iron unites with a considerable number of other elements, metallic and non-metallic, and its physical properties as a rule very considerably modified, even by the presence of very small amounts of these combining substances. The elements that are always found associated with iron to form steel are carbon, manganese, silicon, sulphur and phosphorus. All of these elements may be regarded as impurities with the exception of carbon, with which iron unites at certain temperatures to form definite complexes or solid solutions. The carbon gives the steel definite physical properties, and the amount is regulated to suit the purpose to which the steel is to be applied.

Every metallurgist and engineer knows that steel is not homogeneous. The fact is so well recognized that ordinary commercial practice allows a certain measure of segregation to exist. Specifications are sometimes even written in which explicit directions

are given that in test pieces cut from finished material, an increase will be permitted in the allowable content of impurities.

Segregation is one of the inevitable defects of the present method of manufacture. The steel on issuing from the furnace consists of iron, and carbon compounds of iron, associated in a heterogeneous liquid mass, with small quantities of manganese, silicon, phosphorus and sulphur. Every liquid has a definite solidifying point. In the process, each crystal-forming substance, element or compound has a tendency to separate from any substance with which it may be mixed. This tendency results in perfect isolation when the substances have little affinity for each other, and solidify at widely different temperatures. When the rate of cooling is rapid, or when substances have nearly the same solidifying temperature, or when they have an affinity for each other, the differentiation may be so much interfered with that there is no appreciable separation of the components. In addition to the regular separation in obedience to the laws of crystallization, there is a definite process of liquidation and separation on the part of the metalloids which sometimes results in a very impure spot in the center of the mass. The metalloids in different combinations, *i. e.*, the carbides, phosphides and sulphides of iron and manganese, being lighter than the mother metal, rise to the top in the molten state while the purer iron sinks to the bottom. The lower part of the ingot will thus contain much less than the average of impurities since whatever excess is in the top must be taken from the bottom. Although this irregularity may be in part counteracted by repeated heatings and coolings and a great amount of working, it can never be overcome entirely. Steel will not be absolutely uniform, and different rolled sections will give slightly different analytical results.

The fact that plates are not homogeneous when rolled from ordinary ingots may not become evident from the usual inspection, since the test pieces are generally taken from the corners or edges of the sheet, but even so, the variations are by no means unimportant. Results of recent investigations bearing on homogeneity showed much irregularity between different parts of the same plates, *i. e.*, marked differences in carbon, phosphorus and sulphur content between test pieces taken from the edge and center of the same plates from ordinary plate ingots.

The summary of a study of segregation in steel shows that it is ever present, that the extent of the concentration bears a relation to the proportion of impurities, that manganese does not apparently segregate to any extent, but that certain portions of finished material will contain a higher percentage of carbon, phosphorus and sulphur than will be found in the test pieces cut from the edge of plates and bars. If a low carbon steel is low in phosphorus and sulphur (0.05 per cent. or below), segregation is not liable to occur, and a fair degree of uniformity for practical purposes may be expected.

It has long been known that metals which have a complex structure are far more subject to corrosion and decay than those which are comparatively homogeneous. Concepts of molecular physics offer a simple explanation for this fact, and incidentally unfold a reason why steel structures fail in time. The view is based on the principle that the alteration of the state of a heterogeneous substance is produced through the eccentricity of the molecular motion. The molecules of homogeneous solids are in regular vibratory motion about a point of equilibrium. Equilibrium denotes a state which is independent of time. The possibility of such a state is dependent on the homogeneity of the system. In heterogeneous bodies, equilibrium cannot exist and the system will change spontaneously into a homogeneous state, a process that will be greatly accelerated if the initial state of the system be modified by some preliminary impulse, such as rise in temperature, mechanical agitation or electric action. All heterogeneous systems (of which steel is an example) are, as regards their internal molecular motion, in a condition of unstable equilibrium, and this internal stress is a ceaseless attempt to attain homogeneity. Work is being done by the system to reach this state. The same amount of work was performed in making it a heterogeneous system. The struggle to regain homogeneity may manifest itself in various forms of energy, *i. e.*, heat, electricity or chemical action, the outcome of which is the physical and chemical transformation of the system.

Illustrations of the widely applicable principle thus briefly stated are not wanting. The failure of steel bridges is no doubt often due to the gradual progress of molecular changes going on in these structures. The phosphorescence of alkaline earth

sulphides containing a trace of impurity is entirely analagous to the decay of steel through its own energy, *i. e.*, an instance of the energy developed by a heterogeneous system in the effort to re-establish its homogeneity. From the apparent capacity of solid substances to diffuse into each other, which, though slight, is undoubtedly true, it follows that mutual chemical reaction may take place in heterogeneous solid systems, and that ultimately a condition of homogeneity or equilibrium will be established. During the process, however, such systems respond to slight changes in external conditions with the result that local chemical decomposition cannot be entirely prevented.

It has already been pointed out that heterogeneity was an important contributary cause of intense local action as manifested by "pitting" in underground steel water mains. The occurrence of electrolytic activity in the absence of outside currents, in the Rochester steel conduit, leads to the discussion of the theory by which this dangerous form of corrosion is accounted for.

Electro-Chemical Theory.—We do not yet understand the true nature of electrical phenomena. Whether the electric current consists of the flow of a continuous fluid, or is the outward manifestation of localized transformations of electro-magnetic into heat energy, as under Maxwell's theory seemed probable, or is merely a condition of the ether, we know not. But we know that electricity is omnipresent on this planet, and exists everywhere, even between the molecules of solids, liquids and gases, and through the space to the stars. We know of it as an invisible cause, producing various manifestations of energy, and generally rendered active by some molecular disturbance such as friction or chemical action. In no branch of knowledge have greater difficulties been encountered than in formulating an all-embracing theory for the bewildering variety of facts and discoveries relating to this intangible agent of change. According to the latest and widest scientific generalization, electricity is a kind of subtle fluid with an atomic structure, consisting of electrons or very small corpuscles. The theory reduces all electric and magnetic phenomena to the distribution and motion of these electrons, and whatever relation they may bear to the ether, they are also the units from which are built up the atoms of ordinary material elements.

The electron theory will probably pass like Maxwell's great theory and the rest, but it must be said that it has been pre-eminently successful in unifying and co-ordinating the most diverse phenomena in electricity and magnetism in such a way that all may be interpreted in terms of one simple and fundamental conception, a concept indeed that bids fair to lighten the darkness that obscures the most elusive and mysterious of all natural phenomena.

In science no theory is final, simply because we can never really understand the true nature of things. With the aid of theory we peer into the mists and endeavor to take bearings while in search of scientific truth, but end by merely recognizing the limits to attainable knowledge. The late Lord Kelvin admitted sadly, when near the end of his long life spent in the study of electricity, that he knew no more of the real nature of electrical phenomena than when an undergraduate in the days of Michael Faraday. And so perforce, for the discussion to follow, we must go back to that great man, who was endowed with an insight into nature like a god, with a vision that enabled him to see beyond the mists, and whose laws form the basis of the accepted views of electro-chemistry today.

Early in the 19th Century, Berzelius, from prolonged study of the electrolytic decomposition of neutral salts, enunciated the theory that all chemical action was the result of electric forces between oppositely charged atoms. Later, Faraday affirmed that electricity and chemical affinity were one and the same. According to Faraday's law, all movement of electricity in electrolytes occurs only by concurrent movement of ions, and in the following manner: Equal quantities of electricity move chemical equivalent amounts of the ions. Arrhenius now asserts that only electrically charged ions can react chemically. Thus it will be seen that electrolytic and chemical action are very closely related. Indeed, it may be assumed that only that portion of a body is chemically active which is electrolytically active, and that ionization is necessary for chemical activity, just as it is necessary for electrolytic conductivity.

The phenomenon of ionization is not fully understood. In thermal dissociation, the great velocity with which the atoms of a molecule vibrate separates them to such an extent that they

no longer exist as molecules but as ions, which are to a certain extent independent of each other, but not electrically charged.

In electrolytic dissociation, ionization is apparently due to some specific power possessed by the solvent by virtue of which it is able to overcome the electrostatic attraction existing between groups of molecules and separate them into ions. Concerning the nature or mechanism of the process we can only surmise, but a direct parallelism has been found between the dissociating power and the dielectric constant of solvents. If the forces holding the ions together in a molecule are electrical in their nature as now believed, it follows that they will be much weakened by interposing a dielectric or immersing the molecule in a medium of high specific inductive capacity. The mutual electrostatic attraction between two oppositely charged bodies is proportional to the dielectric constant of the medium. The greater the dielectric capacity of a solvent, the greater is the degree of electrolytic dissociation of substances dissolved in it, when the conditions are otherwise the same.

Water, for example, is not only the best electrolytic solvent known, but also the body of the highest specific inductive capacity (dielectric constant), and this property, to whatever causes it may be due, will reduce the forces between the electric charges in the neighborhood, and therefore enable the ions to separate. The ions are associated with very large electric charges, and whatever their exact relation with those charges may be, it is certain that the energy of a system in such a state must be very different from its energy when unelectrified.

Arrhenius discovered that those substances, and only those which give abnormal osmotic pressures, are capable of conducting the electric current; and if these substances are dissolved in any other solvent in which they act normally, they lose that power. The capacity of dissolved substances to conduct the electric current assumes a polarized cleavage, a decomposition into positively and negatively charged ions. In addition to the electrically dissociated molecules there exist in the solution undecomposed molecules which are electrically neutral. Only the dissociated molecules are instrumental in current conduction. We must assume, therefore, that all substances that conduct electricity electrolytically are ionized. The actual existence of free ions

in electrolytes, the fact that they bear charges of electricity, and that they migrate under the influence of electric force, was experimentally demonstrated by both Oswald and Nernst. It is the movement of these charges which constitutes an electric current in an electrolyte.

Electrolysis.—If two dissimilar metals are brought into contact, a flow of electricity results from one to the other, caused by the effort of nature to equalize potentials and attain equilibrium. The contact need not be direct. Ostwald has shown that when a metal and an electrolyte are in contact they generally possess a varying difference of potential. A suitable connection, therefore, such as moist air, or liquid containing ions, will serve as a conducting medium and enable the action to take place, the space in between constituting what is known as the field of force.

The theory of the electromotive activity of the ions is now generally accepted. According to existing views, corrosion is an electro-chemical process and can be readily explained under the modern theory of solutions. Owing to the differences of potential, the surface of the metal establishes a flow of current by means of an electrolyte. In order that rust may be formed, a metal must first go into solution and hydrogen given off in the presence of oxygen or certain oxidizing agents. This presumes electrolytic action, as every metallic ion that appears at a certain spot demands the disappearance of a hydrogen ion at another. There is no actual lower limit to the potential difference at which the process will not occur, provided the surface of the metal is not in the passive state.

Every metal possesses a specific electrolytic solution tension with regard to water or a selected solvent, and will continue to go into solution until the osmotic pressure counterbalances the solution pressure. The solution pressure of each metal is also locally affected more or less by physical properties, segregation and surrounding conditions, e. g. crystal form, impurities, temperature and the medium with which it is in contact. In the non-homogeneous metal steel, it has been demonstrated by experiment that different portions of the same plate even a few inches apart or less, possess different solution tensions, and consequently show measurable differences of potential, if connected through a suitable medium. If immersed in an ionized solution,

portions of the same plate behave like different metals. As soon as an electrolyte in contact begins to overcome unequally the solution tension of two adjacent portions of the steel, electromotive force is generated and a current set in motion with the metallic surfaces as electrodes, and the electrolyte as a medium for the migration of the ions. The chemical changes which are brought about at the electrodes by the ions are spoken of as electrolysis.

An insight is here afforded of the mechanism of the current producing process, which arises from the solution and precipitation of the limiting surfaces of the metals of the electrode. The passage of the galvanic stream from the metallic electrode into the solution is, according to circumstances, either associated with the solution or else with the separation of the substance in solution and its deposition on the electrode. Faraday attrib- ferrous ions liberated at the anodes undergo secondary chemical processes present, and transferred the cause of the production of electricity to the places at which these processes occur, *i. e.*, the point of contact between the metal and the electrolyte.

In the electrolysis of iron or steel embedded in the earth, the ferrous ions liberated at the anodes undergo secondary chemical changes in the presence of alkaline salts or dissolved oxygen, resulting in hydrated ferric oxides, or the compounds found by analysis in rust pits. The chemical reactions by which the secondary products are formed occur with a speed which is infinitely great in comparison with the other processes.

Electrolysis occurs as a natural process in buried iron and steel pipe where inadequately protected, provided the ground conditions afford media for solution and electrolytic conduction. A number of instances have established that in the presence of a minute amount of soluble salts in wet soils, normal electrochemical action may produce current enough to be very destructive in time. Wherever the action starts, it is continuous, unless the initial conditions are modified. Precisely these influences are found in the steel conduit at Rochester, and electrolysis from natural causes resulting in serious damage is the outcome. Along the surface of the pipe there exist under the conditions what are called galvanic elements, *i. e.*, chemical systems in which the transformation of energy associated with the changes of

matter succeed in producing electro-motive activity. It is now recognized that the chemical reactions which take place between the metal and the electrolyte furnish all the energy ncessary for the production of the electric current. In the presence of the electrolytes of the wet soil, minute differences of structure or impurities in the plates form with the steel miniature voltaic cells. The chemi-electromotive force generated starts currents flowing around in short circuits from the steel through the electrolyte, to the foreign particles, and back to the steel again. The impurities form with the positive element minute voltaic couples, and thus direct the corrosive action of the electrolyte to the portion of the plate near them. Wherever the current leaves a plate to pass into wet soil, electrolytic corrosion must take place. A steel pipe is ordinarily not in uniform contact with the surrounding soil owing to the coating and other causes. The current leaves where the contact is good, or at points where the least resistance is offered to its passage. This is a reason why the corrosive action is concentrated in spots, and the phenomenon of "pitting" occurs. The rate of change in the corrosion or "pitting" process can be expressed as a mathematical quantity according to the law of Faraday: The quantity of electricity that suffices to deposit one electro-chemical gram equivalent is $\frac{1}{1.035} \times 10^5 = 96{,}500$ coulombs (ampere seconds).

Electrolytic action will take place wherever a current of electricity leaves a conductor which is capable of being oxidized (such as steel, iron, or lead water pipes), and passes into some other conducting medium in the presence of damp or wet soil, except in cases where the current passes directly from one metal conductor to another by direct metallic contact. Thus it will be found that wherever a current of electricity leaves a line of water pipe and passes into the surrounding earth or water, either to follow some other path or to return to the pipe after passing some obstacle offering electrical resistance, such as a piece of slag, or an imperfect joint, electrolytic action will occur, depending upon the volume of the current leaving the pipe. This corrosive process will result in more or less rapid eating away at the point where the current is leaving, which, if not checked, will in time cause the pipe to fail.

It was long believed that a voltage below 1½ volts could not

produce corrosion, since it was below the dissociation voltage of water. This is a mistake, however, because when a current passes from iron through ground to iron and produces corrosion, the counter electro-motive force is only a fraction of a volt. It has been experimentally proved that a small fraction of a volt (a mere directive force in the nature of electric pressure) will produce enough current to cause electrolysis with the conditions generally present with underground pipes. Minute quantities of free carbonic acid or chlorides are nearly always present in the soil, and either of these substances render metallic surfaces "active." The chemical processes previously described are capable of yielding ample current to start corrosion in wet soil, and this action of itself replenishes salt required for electrolytic conduction. The amount of corrosion depends upon both the strength of the current and the time during which it acts. The actual damage is very much dependent upon whether the exit of the current is concentrated in a small area or distributed over a large area. Experience, as at Rochester, shows that electrolytic corrosion ordinarily takes place in spots, producing pittings in the pipes, which indicates that the current leaves the pipe at these spots only; pipes are in this way much more quickly destroyed than if the corrosion took place uniformly over the entire surface.

"Pitting" and "tuberculation" are the forms in which corrosion is commonly manifested in iron and steel water mains. The phenomena of both are due to one principal cause—the solution and precipitation of the metal locally, as a result of electrochemical action. If the current (from whatever source) leaves from the outside of the pipe to pass into the soil, for reasons previously given, electrolytic action is manifested in the form of pits. But if the current passes from the interior of the pipe, tubercles covering pits usually develop. Owing to more uniform electrical conditions over the interior surface of pipes, the action is less concentrated, and thus serious damage from tuberculation rarely occurs.

The term "electrolysis," in connection with underground metallic structures, has often been confined to the corrosion which could be traced directly to outside currents of electricity, commonly called earth currents, stray currents or returns from rails.

There have been many instances near cities of destruction of underground water pipe by currents from these sources. In the study of the corrosion of the Rochester steel conduit, precisely similar results were observed where the effects of stray currents are completely excluded. The familiar soft spots that occur as the result of electric currents were found in the steel pipe, where the presence of return currents is out of the question. The chemistry of the corrosion process going on in the Rochester conduit is precisely the same as in ordinary electrolysis due to return currents from rails or industrial sources. The difference is that at Rochester we have electrolysis in which chemical action is the *cause* of the current, whereas in the presence of return currents, the chemical action is the *effect* or *result* of the stray current, from whatever source. To the former phenomenon of corrosion, in the absence of outside currents, the writer has given the name "auto-electrolysis."

An important conclusion from these studies is that the chemical action of rusting and the electro-chemical process of electrolysis are practically one and the same, and the circumstances which promote or prevent rusting, favor or hinder electro-chemical action. The difference in the two processes is simply one of degree. Stray currents merely accelerate corrosion or render it more energetic. Pipes attacked chemically are not readily distinguished from those attacked electrolytically. If outside currents are of high voltage the destruction may be very rapid indeed. In auto-electrolysis the current generated is usually feeble, and though the corrosive action is slow by comparison it is nevertheless destructive in time.

At Rochester, the ground conditions were such as to bring about corrosion quite apart from outside currents. Since soil influences determine whether pipe will be corroded or not, maps may be prepared from a chemical and physical survey of areas through which pipe is to be laid, which will accurately demarcate harmless and dangerous zones, and in the absence of perfect insulation, the areas in which damage by corrosion would with certainty occur.

The Northern Half of the Conduits.—According to the reports of the engineer in charge, only a small portion of the northern half of the conduit has been affected by corrosion, and this for

a distance of less than ⅔ of a mile, in low, wet ground, mainly through a cedar swamp. Fourteen rust leaks occurred here, between 1903 and 1907, which were repaired, and the pipe was re-coated in the manner previously described through this small area.

The better conditions existing in the northern half of the conduit are, no doubt, chiefly due to the more favorable soil influences there. This portion of the pipe is generally laid through sandy loam, from which water easily drains away naturally, while much of the southern half of the pipe is laid in clay more or less saturated with water. It is probable, moreover, that the Sabin japan coating afforded a better protection than the asphalt pipe dips given the southern half of the pipe. For years after this process was applied it was believed that an ideal method had been found of protecting steel water mains. While apparently more durable by several years than the asphalt pipe dips, the Sabin japan coating proved to some extent a disappointment at Rochester. Where the soil influences were really severe, as in the cedar swamp, the coating gave way, as evidenced by the number of rust leaks, and but for the pipe being promptly uncovered and recoated, disastrous consequences might have followed.

Conclusions.—(1) Electrolytic action occurs naturally to a greater or less extent in iron or steel structures embedded in the ground, unless protected from the access of water. Even in the best or most homogeneous steel there are contiguous areas of different electrical potential, and if an ionized solution (*e. g.* soil water) remains in contact with the metal, corrosion takes place in accordance with the laws of electrolysis.

(2) The corrosion of the Rochester steel conduit was caused by electrolysis, the current for which resulted from chemical processes between water solutions in the soil and the metal.

(3) The trouble was confined to areas in which excessive moisture was normally present, or where the soil was wet for considerable periods. The soil water in contact with the steel produces chemi-electromotive force from electro-chemical action, and the electrolytic damage is proportional to the time during which the current acts. In the sandy, or well drained soils, ex-

cessive moisture is not in contact with the metal long or continuously enough for the feeble current to give rise to damage.

(4) The actual damage from electrolytic corrosion depends upon whether the exit of the current is concentrated in a small area or is distributed over a large area. If the current leaves the plates in spots (owing to breaks in the coating, or local irregularities in the steel) the pipes are much more quickly destroyed than if the corrosion takes place uniformly over the entire surface.

Electrolytic surveys which consist of voltmeter readings are not sufficient to determine the existence and extent of electrolytic corrosion. Direction and strength of current flow in various parts of the system are required in addition to the voltage readings.

No general laws can be laid down as to resistance of iron or steel against corrosion, as this depends upon composition, structure, accidental causes and the surrounding conditions of exposure. At Rochester, it was found that serious damage by corrosion in the steel main ensues where three conditions meet:

Ineffective protective coatings,

Irregularity of structure and composition of steel (an inherent property even in the best steel),

Wet soils.

Iron offers so little resistance to corrosion that there are almost no circumstances of service in which it can safely be placed without some means of guarding against deterioration. While the usual bitumen coatings no doubt delay corrosive action, the protection afforded, as shown at Rochester and elsewhere, is not durable in wet soils. For such severe conditions, no permanently effective coating has been discovered.

Irregularity of structure and composition of steel (giving rise to surface differences of potential) cannot be entirely prevented. This fault, however, may be greatly lessened by care in manufacture, by cutting down impurities to an irreducible minimum, and by rigid inspection, rejecting all plates showing scars, scratches, or evidences of segregation.

The conclusion is thus reached that the most efficacious measures to be observed for prolonging the serviceable life of steel water mains lie in modifying the ground conditions (wherever

excessive moisture exists). This may be done by surrounding the pipe with sand and gravel, by avoiding the maximum water level, by drainage, and by avoiding, as far as possible, laying steel mains through wet areas.

Other Steel Conduits.

The principal deduction from the study of the corrosion of the Rochester steel conduit was that ground conditions play the leading part in determining the serviceable life of steel water mains, and that the most effective means of guarding against deterioration is in controlling or modifying these influences where known to be severe. Since it is unsafe to draw sweeping conclusions from a single instance, it was deemed advisable to collect data concerning other steel conduits for comparison. The opportunity was not afforded of observing precise conditions, but essential facts were secured through correspondence with engineers of eight different supply systems, where steel mains had been for a number of years in service. Replies were received from the following cities and water companies: Portland, Oregon; Atlantic City, N. J.; Cambridge, Mass.; New Bedford, Mass.; Allegheny, Pa.; Pittsburg, the East Jersey Water Company, and Minneapolis. The information obtained related to the character of the steel used, the coating or method of protection, the character of the soil, the nature of the corrosion, if any, and the extent of deterioration. Only a brief synopsis of the reports received will be given.

The Portland Steel Conduit.—A nearly parallel case of corrosion exists at Portland, Oregon, to that at Rochester, although the damage sustained is not so great. The writer must acknowledge indebtedness to D. D. Clark, Esq., engineer of the Portland Water Board, for a very complete and interesting account of the trouble there.

The Portland steel water supply conduit was laid in 1893-4 and is about 24 miles long. The average diameter of the pipe, the thickness of the plates, the specifications for the steel, and the asphalt coating, all agree very closely with the same features of the Rochester conduit. The pipe trench averages 6½ feet deep, and the soil is mostly of a clayey character, with occasional wet

areas. Damage from corrosion became manifest 10 years after the pipe was laid, and leaks in the plates began to appear. The pipe was uncovered at these points, and underneath the rusty looking clay which adhered to the top of the coating, numerous pits were discovered. Analysis of the soil failed to show the presence of corrosive constituent. Nothing is said of outside sources of electricity, electrolysis from "stray" currents apparently being out of the question. The points where the principal leaks have occurred are from 12 to 14 miles from Portland where the soil in which the pipe is buried is a yellowish, sandy clay. The surface of the ground here has a slight slope transversely to the line of the pipe, and in consequence, water accumulates in the trench to some extent. The water in conjunction with the clay is supposed to be harmful, since it is noticed that at other points where the same quality of clay exists, but the water is not so abundant, the corrosion is much less apparent. Mr. Clark calls attention with emphasis to the condition of the pipe where buried in sand; no pitting of plates observed, and but few spots of rust.

After the occurrence of a number of leaks in 1905, the conduit was uncovered at twenty different points, aggregating a length of 590 feet. Only the upper half of the pipe was examined, but pittings large and small, found and counted, numbered 1088. Many of these pits were ¼ inch in diameter and some were so near the point of breaking through, that they were plugged before refilling the trench. In some places the clay was quite wet, and water accumulated in the trenches when opened. The pipe was found to be in the worst condition where the clay was wettest.

At a point where the pipe was laid in gravelly soil which allowed surface moisture to readily drain away, no pits, and but few signs of rust were found, and the coating was in fair condition. The same was found to be true in a river bottom, where the trench was entirely in sand; here the pipe was in excellent condition, with no pitting in the plates, and only a few rust spots around the rivet heads.

All pipe sections examined in sandy or gravelly soils appeared to be in a fair state of preservation, and afforded a striking contrast to the damaged state of the pipe wherever uncovered in wet clay soils.

After a careful investigation of the corrosion of the steel conduit, Mr. Clark concluded a report to the Portland Water Board with the following statement: "The indications are that the trouble is due to the nature of the steel of which the plates are made, and the readiness with which it is corroded by the action of soils and water; and hence the insufficiency of the asphalt coating is largely a contributary cause."

The corrosion of the Portland conduit is very similar to that at Rochester, and is probably due to the same causes. It is but another case of auto-electrolysis. The electrical conditions are apparently more uniform in the Portland conduit, and the points of exit for the feeble current generated along the surface of the pipe more numerous, which accounts for the great number of pits. The intense local action being thus less concentrated, the actual damage has progressed more slowly.

Atlantic City.—The earth and water of salt marshes near the sea or adjacent to estuaries are actively corrosive to buried metallic structures. A typical example is found in the 30-inch steel water main of Atlantic City, N. J. This conduit was coated with mineral rubber, and laid in 1901 (about 5 miles), through a salt marsh. The engineer and superintendent, Mr. Van Gilder, gives few details, but writes that the pipe is rapidly deteriorating.

A verbal statement from an officer of the New York and New Jersey Water Company represented similar conditions of steel pipe corrosion where one of their mains was laid through a salt marsh. It has been observed that clay soils impregnated with salt or brackish water are much more corrosive than sandy soils similarly situated.

Cambridge, Mass.—The corrosion of the 40-inch pumping and distributing main of Cambridge by electrolysis from "stray" currents has been carefully studied, and the results are too well known for repetition. The specifications for the steel were the same as at Rochester, and Portland, and the Sabin process was used for protection. It is worthy of remark that the greatest damage was wrought where the soil was a moist, sandy clay. It is therefore probable that the function of outside currents was merely to hasten greatly a process that would have occurred naturally in time.

New Bedford, Mass.—The 48-inch steel main of New Bedford, consisting of soft steel coated with the best quality of asphaltum, is 8 miles long, and has been in service about 10 years. The soil in which the pipe is laid is generally of drift formation, and is chiefly composed of gravel, sand and boulders. Two miles of peaty swamp was passed through, into which gravel was hauled to cover the pipe. No trouble from corrosion. Peat is said to be non-corrosive by some authorities.

Pittsburg.—The 42-inch steel main laid for the water supply of Pittsburg, in 1902, consists of open hearth steel plates. Mineral rubber coating was used for protection. The soil through which the pipe passes varies from shale and clay to sand and gravel formation. Trouble from corrosion has only occurred in one locality, near the power house of a street railway, where one leak and a number of deep pits have developed. The action is attributed to outside currents, and in order to arrest it, the pipe line system has been connected directly with the bus bar generator in the power house, making the pipe line negative to the railway tracks. It is of interest to note that the bitumen coating failed to prevent electrolysis, whatever may have been the source of current.

Allegheny, Pa.—The steel for the Allegheny water main was made by the open hearth process, the specifications being very similar to those for the Rochester and Portland conduits. The pipe was coated by the Sabin process, and passes through a sandy loam and shale rock soil. No evidence has appeared of exterior corrosion; the interior of the pipe has not been examined.

Minneapolis, Minn.—The water main laid in 1898 is of mild steel, and was coated with "Mineral Rubber." The pipe is embedded in hard, yellow clay. The soil is damp in places, but nowhere could it be called wet. No water developed in the trenches. The pipe has been examined in a number of places and found in good condition.

East Jersey Water Company.—The steel main of this company has been in service since the early nineties, and is often cited as having given no trouble from corrosion. Bitumen coatings were used for its protection. General features of the soil as described by an engineer formerly connected with the company

would suggest conditions which are not generally corrosive. The soils have weathered from the glacial drift overlying that region, and range in character from thirsty, gravelly uplands, to sandy, alluvial loams in the lowlands. Some tuberculation has occurred on the interior of the pipe, but wherever the exterior has been exposed, it was found in good condition.

The Durability of Steel, Wrought Iron and Cast Iron.

This subject can only be discussed very briefly.

There is a wide divergence of opinion among metallurgists on the corrodibility of the various forms of iron. Experience at Rochester, Portland and elsewhere, seems to show that cast iron resists corrosion better than any other form of iron, and wrought iron is less easily corroded than mild steel. As between steel and wrought iron, some metallurgists claim that the difference is slight, but their reported experiments have not been carried far enough to base a final opinion. The corrosive influences of nature can never be precisely imitated, and moreover, the time during which laboratory experiments extend is relatively so short that they are of little value compared to actual experience. Besides, practical experience on such subjects is always more reliable than mere laboratory experiment.

Several instances are related of steel bridges in New England and the West, erected during the last quarter of a century, that have already become unsafe from corrosion, while similar neighboring wrought iron structures twenty years longer in use, are standing apparently unimpaired. There is a prevalent and widespread conviction among engineers that steel corrodes much more rapidly than wrought iron, and while the opinion may not rest on experimental evidence, the reasons for it are sound. Wrought iron differs from low carbon steel, in that the latter is free from slag, and the former contains only a trifling amount of manganese. Wrought iron consists essentially of a metallic matrix identical with low carbon steel, in which is mechanically mixed a small quantity of slag. The slag is far from unimportant, and probably accounts for the resistance wrought iron offers to corrosion. It is the characteristic component of wrought iron, which usually contains from 0.20 to 2.00 per cent. by weight, and often

as much as 4 per cent. by volume. In composition, it is a basic ferrous silicate, and is present simply because this variey of iron is made by welding together at high temperature, pasty granules of iron in a bath of such slag, without subsequently melting the resultant mass, or in any other way giving the envelopes of slag imprisoned a chance to escape completely. Wrought iron is not a definite thing by any means. Its character depends upon chemical composition, and this in turn upon the composition of the pig iron from which it is made, and the care and skill with which the operation of manufacture has been conducted. The five elements in pig iron affecting it, are silicon, carbon, manganese, phosphorus and sulphur. Experience has shown that the more nearly steel approaches a pure iron, the longer it resists corrosion. The properties of wrought iron are the nearest approach to those of pure iron of any commercial material, notwithstanding its slag. This is because the slag is mechanically mingled, and does not interfere with the chemical or physical properties of the product.

On account of the honey-comb structure of wrought iron, and the fact that many of the globules of iron are encased in thin silicious shells, which are non-conductors, the electrical resistance offered is sufficient to prevent damage from feeble currents generated along the surface of a pipe. The slag content affords the same kind of protection to cast iron. In limiting electrolytic action, the units of iron enclosed in silicious shells behave like water-tight compartments in a ship; owing to the small surface exposed, the current arising naturally is not of sufficient intensity to produce destructive effects. Neither cast iron nor wrought iron resist outside currents of high voltage, although damage by electrolysis proceeds more slowly than in steel. A reason why steel yields more quickly to electrolytic action is that the combined carbon forms with the iron a complex ion, and is carried with it in the direction of the current, while the dissolved carbon and graphite in cast iron are not carried with the current, but remain as a muddy deposit at the anode, arresting the action.

An important advantage of wrought iron is its rough surface to which paint or other protective coatings will adhere more firmly than to the comparatively smooth surface of steel. Other qualities of wrought iron which tend to make it less corrodible

are the absence of blow holes, and the comparative absence of manganese, which is now believed to be an important source of electrolytic activity in steel.

The serviceable life of cast iron, wrought iron and steel structures cannot be determined, although by deduction it may be approximately estimated. It would be useless and misleading to attempt to establish any rule, the circumstances and conditions being so dissimilar. From England and France data have been obtained concerning the durability of cast iron and wrought iron as materials of engineering construction, and this may afford means of forming a fair estimate of the endurance of steel. The first cast iron bridges were built in England about 125 years ago. Wrought iron bridges were first constructed about 60 years later. Thus we have evidence of cast iron structures that are said to be not deteriorated from visible corrosion after more than a century of service, and wrought iron plate bridges after 60 years.

Examples of great durability of cast iron water pipe have recently been published. M. C. Cavallier, director of the foundries at Pont-a-Mouson, France, gives some interesting records of long service of cast iron water pipes. Recently the first pumping station for supplying Paris with water was discontinued. The intake pipe extending out into the River Seine, being of no further use, was taken up. It was laid in 1802, and consisted of flanged iron pipes. After an immersion lasting over a century, these pipes were in such good condition that they might have been relaid, but being an obsolete type, were broken up and remelted. After removing the scale from the exterior, the words "Creusot an 10" could be read.

Cavallier also mentions a number of ancient cast iron pipe lines which are still in use. The conduits which supply the water to the great fountains at Versailles date from the same period as the park itself. Five pipes, 20 inches in diameter and 1,000 feet long, were laid in 1685, or 222 years ago. Several more pipes of various sizes, having in all a length of about 5 miles, were laid between 1668 and 1688. All the lines at Versailles are made of pipe one meter in length, with bolted flanges. These pipes still serve their purposes satisfactorily, and the few repairs which have been required have generally been necessitated by the condition of the flange bolts.

In Clermont-Ferrand there is a line of cast iron water pipe that was laid in 1748, or 160 years ago. These pipes are 0.5 to 0.8 inch thick, according to the pressure in the different parts of the line. The system is said to be still in operation under considerable pressure.

Other instances were given of cast iron pipe in service more than a century. Whatever method may have been used to protect these old French pipe lines had long lost its efficiency. The evidence here presented would indicate with proper precautions, no practical limit can be given to the endurance of cast iron pipe.

The use of wrought iron for large steel water mains is of comparatively recent origin, beginning since the middle of the last century. Pipes laid during this period have given satisfactory service, with no serious trouble from corrosion, except from occasional cases of electrolysis due to outside currents. The durability of wrought iron will be better appreciated when the thinness of the plates is considered.

The application of steel to large water mains is of such recent origin that it may be considered to have scarcely passed the experimental stage, having begun only about 20 years ago. From careful study of information concerning ten steel water mains, subjected to dissimilar influences in various parts of the United States, the conclusion is reached that except where soil influences are severe, the serviceable life of these structures will endure throughout the periods for which they are intended. It was previously recommended to modify ground conditions where severe. If this should prove impracticable, it would then be wise to substitute cast iron or wrought iron pipe in all wet areas.

DISCUSSION.

President Burgess: I agree with this speaker that he has been dealing with one of the most important subjects before the electrochemist. We are fortunate in having his complete paper for our records, and it will reach a larger audience than that here present. It is to be regretted that we cannot enter into a detailed discussion of this paper, but in view of the fact that

the author has been greatly limited in the time allowed him perhaps it would not be courteous to invite discussion.

Mr. Richard H. Gaines: The society could not discuss a more useful subject, nor one of greater interest to engineers today. I am associated with a great many engineers, some of the leading engineers of the country, and I know they are lying awake at night wondering what to do in regard to this subject of electrolysis because no permanently protective coating has been found. If somebody will solve the question of the coating, the problem of corrosion would not be so serious.

Mr. Carl Hering: I do not think Mr. Gaines' conclusion is necessarily correct, that because the milli-ammeter does not show a current, that therefore the pitting was not electrolytic and due to the stray currents. A small fraction of an ampere flowing out at one spot will soon corrode through a comparatively thin-walled pipe, and such a small current could not possibly be measured by a milli-ammeter.

Mr. James F. McElroy: In this matter of testing pipes underground to determine whether the pipes are carrying electric current, I will say that the subject is full of difficulties when we attempt to determine the exact quantity of current flowing through a pipe. When, however, we attempt to ascertain whether conditions exist which would cause a current to flow and hence under proper conditions to produce corrosion without attempting to determine the quantitative measurement of the current in the pipe, it seems to me that this can be fairly determined from the difference of the electrical potential of the pipe buried in the earth measured at different points along the pipe system.

Several years ago I made a test to ascertain the potential at different points of a pipe buried in the earth and made use of a feeder belonging to the street railway system which feeder was not in use at the time. This feeder was some four miles long and was disconnected from the street railway system at all points. This feeder was connected to the water pipe at a point not far from the power station and a voltmeter was then used to connect the feeder to the water pipes in different parts of the city. The voltmeter indications gave the difference of potential

in the water pipe between the points tested and the point where the feeder was connected to the water pipe. In this way the difference of the electric potential of the different points of the water pipe was determined and the difference of these potentials measured the electromotive force causing electric current to flow through the water pipe between these different points. The lines of falling potential would indicate the directions in which the flow through the pipe system was taking place and established the fact that there was such a flow through the pipes, even in parts of the city at some distance from the street car tracks. It also indicated that the current through a water pipe system and through the earth in which the pipes are buried, does not follow a straight line back to the power station, but certain tests showed a fall in the potential of the pipe system in lines nearly at right angles to the line connecting the points tested to the power station. In all pipes tested, conditions existed which produced current through the pipes and this current entered and left the pipes at intervals. The changing amount of current used on neighboring traction lines caused a shifting potential on the water pipe. This would naturally cause the points where current enters and leaves these pipes to shift about a good deal. We would expect to find that the corrosion action on the pipe referred to in Mr. Gaines' paper would be found to be widely distributed on account of the shifting potential referred to.

Prof. W. D. Bancroft: It seems to me that one important factor is missing. If you have a solution containing chloride in contact with iron there is going to be rusting. There is one thing we should know and that is what is the difference in the different parts of the steel that causes some places to corrode and others not to corrode. If there is a difference we draw one set of conclusions; if there is no perceptible difference, we must draw another set of conclusions. Until we have these data I do not think we can discuss the matter with much profit.

Mr. Gaines: I could give data of the analyses, I have it here, but there was not time enough to read it.

Mr. Clayton H. Sharp: It seems to me that this paper and this discussion which we have had point out the fact that we have to deal in the case of underground pipe with electrolysis

from two causes which are distinct from each other. In the first place we may have an electrolysis due to the stray currents which are picked up by the pipe and which by it are delivered to moist soil, and in the next case we may have electrolysis due to local voltaic action, which I understand is the case in the Rochester instance described.

I do not quite see how we could detect or measure the currents which are producing the change in the latter case, because the length of the circuit would be a very short one. We have a little spot where a difference of potential is produced, due to some lack of homogeneity in the iron, or some strain, or some of these causes which Professor Burgess pointed out in his address, or due to better contact between the pipe and the soil at that part and higher concentration of the electrolyte. I do not know how we could get at the actual current flowing in that case. In the second case we can get at it.

I wish to call attention to the great possibility of self-deception which lies in the use of the voltmeter in connection with such tests. Tests for electrolysis have been made and widely published in which the most astonishing, most alarming results have been exploited. The tester had in such case taken a voltmeter and connected one terminal to the pipe connection and the other terminal to the rails of the trolley track, and found one-tenth of a volt, or two volts, and then he had taken some kind of a contraption, sort of a wheatstone bridge, and measured the resistance between the rails and pipe, and divided the voltage by the resistance, and said he had so many thousand amperes flowing out of the pipe at this point, and each ampere destroys twenty-five pounds of iron per year, and consequently the whole system of pipes was going to the bow-wows. That kind of a report has been made in a number of cases in this country, and has caused unnecessary alarm and has beclouded and befuddled the whole aspect of the case. It is serious enough as it is, but the use of such false methods of testing as that tend to bring the whole science of electrolytic surveys, as they are called, into disrepute.

It is possible to measure the current flowing along a pipe if it is of any considerable amount, but it must be done with the use of suitable instruments. If you find that there is a difference of potential between two points on that pipe, a sufficient difference of potential, such as is not to be accounted for by fortuitous

contact differences, thermoelectric forces, or some of these things, it indicates a flow of current.

I have had in hand a case, which is perhaps an unusual one, where the cross-section of the pipe was so large that the differences in potential observed were very small, the case of an enormous steel pipe, but it is perfectly possible to detect and locate flow of current along that pipe and not only that, but it is possible to take simultaneous readings of differences of potential on different lengths of the pipe, to see whether current is flowing in or out of the pipe in certain localities, and to measure such in or out flowing current with a sufficient degree of accuracy. That is the kind of method which does not lead to self-deception, but brings out the facts of the case so that we can be pretty sure that where we find by measurements of this kind that current is actually leaving the pipe, and leaving it in the soil, and not by way of some metallic conductor, damage is being done to the pipe. How serious the damage is will depend upon whether the current corrodes the pipe uniformly, so that the decrease in thickness of the pipe is very slow, or whether it is forming pits, in which case the action of a very small current may very quickly produce a leak in the pipe. We have to consider, too, in the study of pipes, that large potential differences may exist between the pipe, and, we will say, the rails of the trolley track, and still not cause any damage, because the pipe is so located that the current cannot very well get out. Take, for instance, the pipes in a very large city, where practically the whole surface of the city is covered with a pavement. The rain water flows off the pavement and does not go down in the soil, so that the soil may be in a fairly dry condition. In that case the indication of the voltmeter may be entirely unreliable, and it is necessary to go, as I say, to the instrument which will tell the small potential differences which may exist between points in the pipe.

Mr. Carl Hering: I am glad that Dr. Sharp said what he did. Professor Bancroft said the corrosion depends greatly on the condition of the iron of the pipes in different places. It seems to me that in the case of underground pipes, it depends even more on the condition of the soil around the pipes, because that is in most cases very heterogeneous as compared with the much more homogeneous pipe.

Dr. H. N. Potter: Electrolysis may arise from differences in chemical composition in the iron. It may doubtless arise from differences in density in chemically uniform metal. It is probably industrially impossible to produce iron structures of such physical and chemical evenness as to escape rusting if exposed to a perfectly homogeneous electrolyte. But the electrolyte will not be homogeneous in any practically important number of cases and therefore in the presence of an electrolyte the prevention of rusting is so improbable as to have only a theoretical interest.

Practically the solution of the problem will be found in eliminating the electrolyte. In my opinion an approximate solution at least may be hoped for along the line of a compound which will stick to the iron, whether the latter is rusty or not, and will be impervious and non-conducting and will stand such abuse and wear as the particular piece of iron must withstand in service. Certain cellulose and linoxyn compounds meet the chemical requirements. Perhaps the new electrochemical point of view may be potent in getting some of them a trial under conditions sufficiently clearly defined to yield valuable results. At any rate, to stop rusting, get rid of the electrolyte.

Mr. Carl Hering: In my opinion this subject of the electrolytic corrosion of buried pipes is so important that I suggest we devote a part of the next meeting to a topical discussion of it. It is one of the most important subjects we have had to deal with as far as the amount of the commercial interests are concerned. There are millions of dollars worth of property underground which may be in greater or less danger of rapid corrosion by stray currents; the action is largely electrochemical and the electrochemist is therefore the one who is best suited to deal with this problem, which is becoming more and more important each year as the stray curents become greater and the corrosion deeper. The apparent indifference of the owners of these large properties to the dangers to which they are perhaps being exposed is surprising. Instead of spending a few dollars to prevent or at least lessen the corrosion, they wait until the damage is done and then spend thousands for repairs.

Insurance companies who are so particular about many apparently trivial details seem to overlook this important factor.

In one case known to the writer, a loss of $50,000 might have been saved by spending a few dollars for properly locating and preventing the electrolytic corrosion before the damage was done. The failure of deeply imbedded anchor bolts and their plates, or of other underground parts of steel in the foundations of structures, may result in incalculable loss of property and lives, and yet this gradual destruction may be going on to-day unknown to the owner or to those whose lives may be involved although it might well be possible to check it or at least retard it by the intelligent application of proper remedies.

Prof. Henry S. Carhart: I have come across exactly this thing Dr. Sharp has been telling us about and have had to oppose it as an expert. It is easy enough, as he says, to measure currents flowing along the pipe, but not so easy to measure currents flowing from the pipe to the earth.

I came across one case where there was a difference of potential, ten thousand feet apart, and on the water pipe, and presumably also in the earth, because we found no appreciable difference between the pipe and the earth, of from twenty to twenty-five volts, at two points, ten thousand feet apart.

Mr. Gaines: I think perhaps it might be interesting to give the analyses of the steel, a very badly corroded length, and of one not corroded.

The analysis of the length which was not corroded is as follows: Carbon 0.13, silicon 0.13, manganese 0.34, sulphur 0.04, phosphorus 0.011.

The analysis of the corroded length is as follows: Carbon 0.13, silicon 0.10, manganese 0.30, sulphur 0.05, phosphorus 0.009.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 2, 1908, President Burgess in the Chair.

ELECTROLYTIC REFINING OF IRON.

By Edward F. Kern.

Even though the electrolytic refining of iron is, at the present time, of no especial technical importance, as is the case with the electrolytic refining of copper, lead, nickel, silver and gold, it presents a very encouraging problem for investigation.

In looking over the literature, it was rather surprising to find that scarcely anything has been published on this subject since 1905. In 1904, Prof. C. F. Burgess and Mr. Carl Hambuechen presented a most interesting paper on "Electrolytic Iron" at the Washington meeting of the American Electrochemical Society.[1] This paper brought forth some discussion at the meeting, and also the subsequent publication of several papers by foreign as well as by American investigators.

Synopsis of the More Important Articles.

Previous to 1880 the electrodeposition of iron was applied technically to electroplating iron upon the surface of engraved copper plates, in order to obtain a hard facing from which a greater number of sharp prints could be made.[2] The electrolytes used were principally solutions of ferrous sulfate, containing varying amounts of either magnesium sulfate, ammonium sulfate, ammonium chloride, potassium-sodium tartrate, or else a mixture of two or more of these. Electrolytes, consisting of solutions of ferrous chloride and ammonium chloride were used to less extent, because the deposits from these electrolytes were less adherent, and also there was some difficulty to prevent the deposit forming as spangles. One of the difficulties experi-

[1] Electrochemical Industry, **2**, 183-185 (1904).
Transactions Am. El. Chem. Soc., **5**, 201-210 (1904).

[2] W. C. McMilliams' Treatise on Electrometallurgy, 1899, pp. 251-258.

enced with all iron electrolytes was the ease with which the iron was oxidized, forming a brown precipitate of basic salt. This was retarded by some electroplaters by adding glycerine, and from time to time, as occasion demanded, sufficient acid to clear the solution. The presence of magneisum sulfate was found to cause smoother deposits, and also to decrease the E. M. F. The anodes were either wrought iron or steel plates, and the vats in some cases were constructed of sheet iron, which is not chemically attacked by neutral ferrous solutions.

Apart from electroplating, Burgess and Hambueschen have no doubt done more to develop Electrolytic Refining of Iron than any other investigators. The electrolyte used by them was neutral ferrous sulfate solution, containing ammonium sulfate, the amount of either salt in solution is not given.[3] The anodes were either wrought iron or steel, and the cathodes were thin sheet iron, cleaned of rust and scale. The electrolysis was conducted at a C. D. of 6 to 10 amperes per square foot, and with an E. M. F. of about 1.0 volt, the temperature of the electrolyte being about 30 degrees C. The current efficiency was approximately 100 per cent. The iron deposited as a smooth, dense crystalline, brittle mass, which was so hard, due to occluded hydrogen, that it was difficult to file, unless previously heated sufficiently high to liberate the combined hydrogen. The purity of the refined iron was over 99.9 per cent. Some deposits were formed three-quarters of an inch thick by continued electrolysis for four weeks. Thicker deposits were difficult to obtain, due to the formation of large nodules which caused short circuiting of the electrodes. Stirring the electrolyte produced smoother deposits, which was also facilitated by previously boiling the electrolyte in order to eliminate absorbed air.[4] The deposits, formed in electrolytes which were not previously boiled, were pitted, due to the dissolved gases collecting as bubbles on the cathode and insulating small areas, finally producing small cavities.

W. W. H. Gee, published in the "London Electrician" of June 24, 1904,[5] that about 1890 he deposited iron from an elec-

[3] Elect. Chem. Ind., 1904, p. 183.
Trans. Am. El. Chem. Soc., **5**, 201 (1904).

[4] Elect. Chem. and Met. Ind., 1906, p. 225.

[5] Electrochemical Industry, 1904, p. 319.

trolyte similar to the one used by Burgess and Hambuechen. No experimental data is given other than that he experienced some difficulty due to the electrodes and the electrolyte being oxidized. This, however, was overcome by carrying on the electrolysis in an atmosphere of hydrogen.

A. Neuburger and N. von Klobukow succeeded in producing solid deposits of iron for analytical purposes.[6] The electrolyte used differed from that of Burgess and Hambuechen in that it contained a large amount of ammonium oxalate and a lesser amount of ammonium sulfate. During the electrolysis, a precipitate of basic iron carbonate formed, but was dissolved from time to time by adding sufficient oxalic acid. The electrolysis was conducted at a C. D. of 1.0 ampere per square decimeter (9.3 amperes square foot) at an E. M. F. of 3.5 volts and at normal temperature. The deposit analyzed 99.9 per cent. Fe. A peculiarity claimed for this iron was that it did not rust.

A. Skrabel published[7] an interesting article on the electrodeposition of iron from several different electrolytes. The solutions used were those of ferrous sulfate, and ferrous chloride, containing respectively the sulfates and the chlorides of ammonium or magnesium. No experimental data is given regarding the percentage composition of the electrolyte, the temperature, the current density, or the E. M. F. of the electrolysis. The main object of the investigation seemed to have been the production of allotropic forms of iron. He succeeded in obtaining two forms, which were distinguished by the names: A-iron and B-iron. The first was produced when an iron anode was used, and the electrolysis was conducted at low current density and low voltage. This modification is of silver white color, compact and extremely hard. When exposed to moist atmosphere it rusted, although not so readily as wrought iron. The B-iron was produced when a platinum anode was used, and the electrolysis was conducted at high current density, and with high voltage. This modification is of a grayish color, less compact and less hard than the A-iron.

W. McA. Johnson was granted a patent (No. 780,191, January 17, 1905)[8] for the electrolytic refining of iron, in con-

[6] Electrochem. Zeitschrift, July, 1904, and Electrochem. Industry, 1904, p. 319.
[7] Zeit. f. Electrochemie, Sept. 23, 1904; Electrochemical Industry, 1904, p. 459.
[8] Elect. Chem. and Met. Ind., 1905, p. 113.

junction with a specially designed vat in which the refining is accomplished. No restriction is made to the electrolyte to use, but mention is made that the electrolyte may consist of ferrous-ammonium chloride, slightly acidified with acetic acid, or another weak organic acid, or else, in case the presence of a trace of sulfur in the deposited iron is permissible, then the electrolyte may be a neutral solution of ferrous-ammonium sulfate. The C. D. recommended is from 10 to 20 amperes per square foot, at an E. M. F. up to 1.5 V, and the electrolyte at a temperature of 60° C., which accelerates the reaction and besides is more economical, as the E. M. F. is reduced with rise of temperature.

S. Maximowitsch, of St. Petersburg, Russia, claims to have obtained flexible solid deposits of iron by using a neutral electrolyte containing ferrous sulfate, sodium sulfate, magnesium sulfate, and from 0.2 to 0.3 per cent. of ferrous bicarbonate.[9] This was prepared by adding sodium bicarbonate to a solution containing 20 per cent. of $FeSO_4 .7H_2O$ and 5 per cent. $MgSO_4 .7H_2O$, until a permanent white precipitate was formed, and which soon changed to a brown color, due to oxidation by the air. The electrolyte was kept in working condition by adding from time to time a small amount of $NaHCO_3$. The precipitate which formed was not filtered off, but was allowed to settle to bottom of the vat. The deposit of iron on the cathode, at the start of the electrolysis was light gray in color, and brittle, but gradually became more solid, and when the electrolyte had been in continual use for about a month, or longer, the deposit formed as a smooth, flexible mass. The C. D. used was from 3 to 6 amperes per square foot, with a current efficiency of 97 to 99 percent. No data is given as to the temperature of the electrolyte and the E. M. F. required. Iron anodes and silver-plated sheet copper cathodes were used. One of the main difficulties with the electrolyte was keeping it in good working condition, as it was so readily oxidized, producing a basic precipitate, which had a tendency to partially collect on the cathode.

Sherard Cowper-Coles invented a process in connection with an apparatus for electrolytically producing bright, smooth iron deposits in the form of tubes, sheets and wires.[10]. The electrolyte

[9] Zeit. f. Electrochemie, Jan. 20, 1905; Elect. Chem. and Met. Ind., 1905, p. 115.

[10] London Electrical Engineering, June 13, 1907; Elect. Chem. and Met. Ind., 1907, p. 291.

is a neutral solution of ferrous sulfo-cresylate, which is prepared by saturating a 20 per cent. solution of sulfo-cresylic acid with iron. The electrolysis was conducted with a C. D. of about 100 amperes per square foot, and at an E. M. F. of 3.25 volts, when the distance between the electrodes was half an inch, and the temperature of the electrolyte was 70 degrees C.

SUMMARY.

The electrolytes which have been most generally used for electrodeposition of iron are neutral solutions of ferrous sulfate or ferrous chloride containing respectively the sulfates or the chlorides of ammonium. Sulfate electrolytes gave more solid deposits than the chloride electrolytes.

The presence of magneisum sulfate in an electrolyte of ferrous-ammonium sulfate caused the formation of smoother iron deposits, and also reduced the E. M. F.

Smoother deposits formed when the electrolyte was continuously stirred.

Pitting of the deposited iron was overcome by previously boiling the electrolytes, in order to liberate the dissolved gases.

Maintaining the electrolyte at a temperature of 60 to 70 degrees C. caused smoother deposits, and also reduced the E. M. F.

Oxidation of the electrolyte was retarded by addition of glycerine, or else by conducting the electrolysis in either a neutral or a reducing atmosphere.

The precipitation of basic salts was prevented by adding, as occasion demanded, just sufficient acid (either an organic or mineral acid) to clear the solution.

The iron was deposited as a hard, brittle, crystalline mass, containing occluded hydrogen, which was liberated by heating the mass to high temperatures, rendering it more malleable. It analyzed over 99.9 per cent. Fe.

Deposits of iron from sulfate electrolytes contained a trace of sulfur.

The C. D. used varied between 6 and 20 amperes per square foot, at an E. M. F. of 1 to 1.5 volts, giving a current efficiency of 97 to 99 per cent.

Electrolytes, which contained organic salts, such as oxalates or acetates, required a higher E. M. F. than those which contained only the mineral acid salts, such as sulfates or chlorides.

Iron was deposited as either allotropic form (A-iron or B-iron) depending upon the composition of the electrolyte, the C. D., and the E. M. F. A-iron is of a silver-white color, compact and extremely hard; it formed in neutral electrolytes, when an iron anode was used, and the electrolysis was conducted at low C. D. and low E. M. F. B-iron is of a grayish color, and less compact and less hard than the A-iron; it was formed when an insoluble anode was used, and the electrolysis was conducted at high C. D. and high E. M. F.

A complex neutral electrolyte consisting of ferrous sulfate, sodium sulfate, magnesium sulfate, and 0.2 to 0.3 per cent. ferrous bicarbonate yielded solid flexible deposits, after it had been used for a month, or more, at a C. D. of 3 to 6 amperes per square foot.

A neutral concentrated electrolyte of ferrous sulfo-cresylate yielded bright, compact deposits of iron, when the electrolysis was conducted at a temperature of 70 degrees C. and with a C. D. of 100 amperes per square foot, at an E. M. F. of 3.25 volts.

Experimental Part.

Preparation of the Electrolytes.

The electrolytes which were selected for comparison were: (a) Solution of ferrous sulfate, (b) Solution of ferrous sulfate containing sodium sulfate, (c) Solution of ferrous chloride containing sodium chloride, and (d) Solution of ferrous fluosilicate.

The fluosilicate was selected, as this iron salt is very soluble in water, and besides it was found last year, during a research on the electrodeposition of nickel, that neutral electrolytes of nickel fluosilicate gave very flexible, bright and smooth deposits.[11] This being the case, it was thought that ferrous fluosilicate electrolyte would act similarly to that of nickel fluosilicate ($NiSiF_6$).

The sulfate and chloride solutions were prepared by dissolving the salts in water, and diluting to such a volume that they

[11] School of Mines Quarterly, 29, No. 4.

contained the desired percentage of constituents, which was decided by the solubility of the salts.

Electrolytes used for a later set of runs were prepared by taking a calculated amount of dilute acid (HCl_2 or H_2SO_4) and neutralizing with iron, in the form of an iron-graphite couple, similar to an electric cell. The iron dissolved slowly when placed alone in the dilute acid, but when it was short-circuited with a strip of graphite, the reaction was fairly rapid, and more so when the solution was heated above 50 degrees C.

(*a*) The ferrous sulfate solution contained 40 grams $FeSO_4 .7H_2O$ per 100 c.c., giving an electrolyte containing about 8 per cent. of iron (8 grams Fe per 100 c.c.). (Solubility: 100 c.c. of water at 20 degrees C. dissolves 48.3 grams $FeSO_4 .7H_2O$.)

(*b*) The ferrous-sodium sulfate solution contained 30 grams $FeSO_4 .7H_2O$ and 21 grams $Na_2SO_4 .10H_2O$ (Glauber's Salt) per 100 c.c., giving a solution containing about 6 per cent. of iron and 3 per cent. of sodium (Solubility: 100 c.c. water at 20 degrees C. dissolves 44 grams $Na_2SO_4 .10H_2O$.) A solution containing 8 per cent. of iron and 4 per cent. of sodium was first prepared, but could not be used, as in a very short time the anode became coated with salt crystals, which prevented the current passing.

(*c*) The ferrous-sodium chloride solution contained 28.5 grams $FeCl_2 .4H_2O$ and 10.2 grams NaCl per 100 c.c., giving an electrolyte containing 8 per cent. of iron and 4 per cent. of sodium. (Solubility: 100 c.c. water at 20 degrees C. dissolves 64.3 grams $FeCl_2 .4H_2O$; 100 c.c. water at 20 degrees C. dissolves 35.8 grams NaCl.) Added 1 c.c. conc. HCl per 100 c.c. electrolyte in order to clear the solution.

(*d*) The ferrous fluosilicate ($FeSiF_6$) solution was prepared by taking a calculated amount of dilute fluosilicic acid, containing 31 per cent. of H_2SiF_6, and neutralizing it with metallic iron, short circuited with a strip of platinum, similar to an electric cell. Temperature of solution was kept between 55 and 65 degrees C., until it was almost neutralized. Below 40 degrees C. the reaction was very slow. (Small amount of free acid was left.) The nearly neutral solution of $FeSiF_6$ was diluted so as to contain about 8 per cent. of iron. It was of light green color,

clear, and did not oxidize so rapidly as the solutions of ferrous sulfate and ferrous chloride. Tried to prepare the solution by neutralizing the dilute fluosilicic acid (31 per cent. H_2SiF_6) with ferrous oxide, but not successful, as the acid was decomposed, giving a gelatinous precipitate of silica intermixed with the basic iron salt.

The fluosilicic acid was prepared by digesting a calculated amount of pulverized quartz in a platinum dish with hydrofluoric acid solution, containing about 35 per cent. HF. The reaction produced sufficient heat to cause the solution to boil.

$$SiO_2 + 6\ HF = H_2SiF_6 + 2\ H_2O.$$

Cooled by adding small amount of water, to prevent loss of SiF_4 by distillation.

The $FeSiF_6$ solution was kept in an ordinary glass bottle, and the electrolysis was conducted in glass beakers. There is scarcely any corrosive action of the solution on glass.

When any of the electrolytes were not in use, they were kept in a stoppered bottle and several pieces of iron wire placed in it, which kept the iron in the ferrous condition.

I. Electrolysis of Ferrous Fluosilicate Electrolyte.

The anodes and the cathodes were strips of sheet wrought iron, which were well cleaned of all rust and scale. The cathodes were lightly coated with vaseline and wiped with a clean rag, leaving just sufficient grease to allow the deposit being stripped. The surface exposed of each electrode was 3 inches by 3.5 inches, or 10.5 square inches.

The electrolysis was conducted in glass beakers holding about 650 c.c. of the electrolyte, using one anode and one cathode. Distance between the electrodes was 1.25 inch.

Results of First Day Run:

Current at start = 1.0 Amp. (C. D. = 14 A. per sq. ft.) E. M. F. 0.94 V. Temp. = 21° C.

Some gassing at the cathode, but scarcely any at the anode.

First hour = 1.1 Amp. (C. D. = 15 A/sq. ft.) E. M. F. 0.99 V. Temp. = 21° C.

Second hour = 1.5 Amp. (C. D. = 20 A/sq. ft.) E. M. F. 1.15 V. Temp. = 21.5° C.

Small amount of SiO_2 had separated.

The cell was placed in a water-bath, and the electrolyte heated to 60° C.

Third hour = 2.2 Amp. (30 A/sq. ft.) E. M. F. 0.73 V. Temp. = 60° C.

Current reduced to 1.5 Amp. (C. D. = 20 A/sq. ft.) E. M. F. 0.56 V.

Fourth hour = 1.5 Amp. (C. D. = 20 A/sq. ft.) E. M. F. 0.72 V. Temp. 45° C.

Deposit began to slightly darken, so reduced current.

Fifth hour = 1.1 Amp. (C. D. = 15 A/sq. ft.) E. M. F. 0.60 V. Temp. = 56° C.

Sixth hour = 1.1 Amp. (C. D. = 15 A/sq. ft.) E. M. F. 0.60 V. Temp. = 50° C.

Seventh hour = 1.1 Amp. (C. D. = 15 A/sq. ft.) E. M. F. 0.58 V. Temp. = 49° C.

Only slight gassing at the cathode.

Current off at seventh hour.

Current passed = 9.2 ampere hours.

1.0 ampere hour theoretically deposits 1.0423 grams Fe.

9.2 ampere hour theoretically deposits 9.589 grams Fe.

Anode dissolves = 9.41 grams = 98.1 + % Current Efficiency.

Iron deposited = 8.24 grams = 85.94% Current Efficiency.

The low cathode efficiency was due to free acid in the electrolyte, causing the liberation of hydrogen, which prevented the deposition of an equivalent of iron.

The deposit was solid, very smooth, dull gray color, and quite brittle.

During electrolysis a small amount of gelatinous silica separated and settled to bottom of the cell.

Results of Second Day Run:

The solution was filtered to remove the precipitated silica, and the electrolysis was continued with the clear solution, at temperature of 45° C.

Current at start = 1.0 Amp. (C. D. = 14 A/sq. ft.) E. M. F. 0.72 V.

First hour = 1.1 Amp. (C. D. = 15 A/sq. ft.) E. M. F. 0.70 V. Temp. 48° C.

Third hour = 1.1 Amp. (C. D. = 15 A/sq. ft.) E. M. F. 0.68 V. Temp. 49° C.

Sixth hour = 1.1 Amp. (C. D. = 15 A/sq. ft.) E. M. F. 0.69 V. Temp. 48° C.

Ninth hour = 1.1 Amp. (C. D. = 15 A/sq. ft.) E. M. F. 0.66 V. Temp. 50° C.

Total ampere hours = 9.8. Iron theoretically deposited = 10.215 grams.

A small amount of gelatinous silica separated and settled to the bottom of the cell.

The deposit was very smooth, solid, very brittle and of gray non-metallic luster. It contained 0.12 per cent. SiO_2.

Anode dissolved = 10.08 grams = 98.69% current efficiency

Iron deposited = 9.63 grams = 94.27% current efficiency.

Results of Third Day Run:

The electrolysis was conducted at ordinary temperature (17° to 21° C.) for six hours with a C. D. of 10 amperes per square foot and at an E. M. F. of 0.98 to 0.93 V. The deposited iron was smooth, but very brittle and of dull gray color, of no better quality than the deposits obtained by the former runs. The electrolyte was also slowly decomposed, giving a gelatinous precipitate of silica; so the use of ferrous fluosilicate electrolyte was discontinued.

II. Electrolysis of Sulfate and Chloride Electrolytes.

The anodes and cathodes were strips of sheet wrought iron, cleaned of all rust and scale. The cathodes were coated with a very thin film of vaseline, so as to allow the deposit being readily stripped.

The surface of the electrodes exposed to the action of the current was in each case 3 inches by 3.5 inches, or 10.5 square inches.

The electrolysis was conducted in glass beakers holding about 650 c.c. of electrolyte, and in each case one anode and one cathode was used, placed 1.25 inches apart.

The temperature of the electrolytes was maintained uniform by placing the cells in a water-bath and heating on a hot plate.

The results of the runs are tabulated in Table I.

When the electrolysis was started there was considerable gassing at the cathode, especially in the case of the chloride electrolyte, so before the comparative runs were made, the current was allowed to pass for several hours in order to neutralize the small amount of free acid and to reduce any ferric salts which were present. The deposits at the start peeled from the plates, but after about two hours' running, the mass formed smooth and did not crack nor curl.

When the electrolytes were brought to proper condition, the cathodes were stripped, replaced in the electrolyte, and the records kept, as tabulated in Table I.

About the only trouble experienced was the slow formation of basic salts, due to exposure of the neutral electrolytes to the atmosphere. This, however, was no great inconvenience, as the solutions cleared on adding five or six drops of acid.

The solutions were kept at constant volume by adding from time to time, sufficient distilled water to make up the evaporation.

The deposits (No. 1 and No. 2) which formed in the sulfate electrolytes were smoother, having less nodules than the deposit (No. 3) formed in the chloride electrolyte.

Deposits No. 1 and No. 2 were more brittle than No. 3; they had the appearance on their surface of being made up of a solid mass if minute rhombic crystals; whereas deposit No. 3 (from the chloride electrolyte) had no apparent crystalline form, but was perfectly smooth with numbers of scattered small protruding nodules, especially along the edges. This deposit was also more flexible than those which were formed in the two sulfate electrolytes.

All three deposits, when heated above 700 degrees C., became malleable, and pieces were bent into ¾ inch circles, without cracking; they, however, broke when beaten together. The deposit from the chloride electrolyte seemed to be more malleable than the others, even after all were heated.

The hardness of the three deposits was compared, by means of a file, with that of electrolytic iron formed in a ferrous-ammonium sulfate electrolyte. It was found that the latter was

Table I.

Electrolysis of Ferrous Sulfate and Ferrous Chloride Electrolytes.

Time in Hrs.	Amperes passing	C. D. per Sq. Ft. Amperes	E. M. F. per Cell. $FeSO_4$ Electrolyte No. 1 Volts	$FeSO_4$ Na_2SO_4 Electrolyte No. 2 Volts	$FeCl_2$ NaCl Electrolyte No. 3 Volts	Temperature of Electrolytes. °C.	Remarks.
Start	1.0	14	1.38	1.18	0.78	15	Gassing at the cathode.
¼	1.0	14	1.06	0.85	0.60	35	
½	1.0	14	0.84	0.68	0.52	45	
1	1.0	14	0.87	0.65	0.48	46	
1½	1.0	14	0.90	0.60	0.52	44	Slight gassing at the cathode.
2	1.0	14	0.92	0.56	0.48	45	
3	1.0	14	0.83	0.54	0.44	47	
3	2.0	28	1.40	0.74	0.68	47	Increased current. All the deposits began to darken, so reduced current.
3½	1.5	21	1.12	0.72	0.60	48	
5	1.5	21	1.10	0.78	0.50	50	All the deposits bright and smooth.
6	1.5	21	1.20	0.83	0.55	35	Discontinued heating, reduced current and let run over night at ordinary temperature.
6¼	1.0	14	0.86	0.66	0.38	30	
18	0.75	10.5	1.18	0.95	0.58	18	The deposits, Nos. 1 and 3, from both the sulfate electrolytes were dark gray and non-adherent crystals along the edges of the electrodes; and in the center of face of electrodes they were hard, bright and metallic throughout. Electrolytes were rather turbid so added 5 drops of conc. acid to each cell. Slight gassing for few minutes.
19	1.0	14	0.96	0.58	0.50	47	Started heating the electrolytes.
22	1.0	14	0.83	0.52	0.48	54	All deposits bright and solid.
26	1.0	14	0.86	0.54	0.50	50	
30	1.0	14	0.85	0.55	0.49	52	Let run over night at 48° to 52° C.
42	1.0	14	0.87	0.56	0.48	48	
44	1.0	14	0.86	0.50	0.42	54	Current off. All the deposits were solid and bright.

somewhat harder, more brittle, and less readily oxidized when exposed to the atmosphere. This difference in the properties of iron deposits formed in electrolytes containing an ammonium salt, suggests the possibility that ammonium ions are absorbed by the deposited iron, or else are decomposed, resulting in the formation of an iron nitride, which is a hard compound. This suggestion is merely made to show the possibility for an investigation to prove whether the harder deposits from an electrolyte, containing an ammonium salt, is due to iron nitride, or to other nitrogen compounds of iron.

The quantity of current which had passed through the cells was 43.9 ampere hours, which should have theoretically deposited 45.76 grams of iron.

The deposits measured about 3-64 inch thick.

No. 1. Weight of anode dissolved in $FeSO_4$ electrolyte: = 45.51 grams = 99.45 + % current efficiency. The weight of the iron deposited = 44.62 = grams = 97.51% current efficiency.

No. 2. Weight of anode dissolved in $FeSO_4 .Na_2SO_4$ electrolyte: = 45.59 grams = 99.63% current efficiency. The weight of the iron deposited = 44.98 grams = 98.30% current efficiency.

No. 3. Weight of anode dissolved in $FeCl_2 .NaCl$. electrolyte: = 45.63 grams = 99.71% current efficiency. The weight of iron deposited = 45.26 grams = 98.91% current efficiency.

III. Electrolysis of Ferrous-sodium Chloride Electrolyte.

Having found that iron deposited from the chloride electrolyte was less crystalline and less hard than that from the sulfate electrolytes, the following run was made for the purpose of producing electrolytic iron for a research.

The electrolyte used contained 28.5 grams $FeCl_2 .4H_2O$ and 10.2 grams NaCl, or 8 grams Fe and 4 grams Na. per 100 c.c.

The anodes were strips of wrought iron 3 inches by 3.5 inches (10.5 sq. in.) and 1/8 inch thick. They were cleaned of scale and rust, and wrapped with two layers of muslin, which was for the double purpose of collecting any residues, and also to protect the anode from oxidation by air.

The cathodes were thin sheets of steel, size 3 inches by 3.5 inches, cleaned of all rust, polished and coated with a thin film of vaseline.

The electrolysis was conducted in glass beakers holding about 650 c.c. solution. They were heated by placing on a hot plate, which was found to keep the electrolytes circulating better than when heated in a water-bath.

The volume of the electrolyte in each cell was automatically kept constant by means of an inverted Erlenmeyer flask filled with water, and provided with a rubber stopper through which extended two ¼-inch glass tubes. One of the tubes reached to the bottom of the electrolyzinc cell and the other was just in contact with the surface of the electrolyte. When the electrolyte had evaporated sufficient to allow air to be drawn through the upper tube into the flask, water would flow into the cell until the electrolyte reached the opening of the upper tube which cut off the air, and checked the flow of water into the cell.

Before starting to take the records, the solutions were electrolyzed for about three hours, using wrought iron anodes and cathodes, in order to reduce any ferric salts present and to get the electrolytes in proper working condition. At the start there was considerable gassing at the cathodes, and the deposits split and curled; but after about two hours' running, the deposits began to form smoothly and to adhere.

When the electrolytes were found to be in good condition, the anodes and cathodes were replaced by the weighed anodes and cathodes, and the records were taken as tabulated in Table II.

All three deposits formed quite smooth, and had no apparent crystallization. They were moderately brittle, and had a hardness of about that of annealed medium carbon steel. After heating to about 800 degrees C., they became quite malleable, and were capable of being hammered double. Small pieces after exposure to the atmosphere of the laboratory for several months were coated with rust similar to a piece of sheet wrought iron which was placed on the shelf along with the electrolytic pieces for purpose of comparison.

The deposits measured about 3/32 inch thick. The record of the current was taken at regular intervals by means of a standardized ammeter, which gave a total of 86.2 ampere hours of current having passed through the cells. Taking the factor, 1.0423 grams of iron per ampere hours, the theoretical amount of iron deposited was 89.85 grams.

Weight of anode dissolved in Cell No. 1 was 89.77 grams = 99.91% current efficiency. The weight of iron deposited in Cell No. 1 was 83.98 grams = 93.47% current efficiency.

Weight of anode dissolved in Cell No. 2 was 89.00 grams = 99.05 % current efficiency. The weight of iron deposited in Cell No. 2 was 84.15 grams = 93.66% current efficiency.

TABLE II.

Electrolysis of Ferrous-Sodium Chloride Electrolytes.

Time in Hrs.	Amperes passing.	C. D. per Sq. Ft. Amperes	Cell No. 1.		Cell No. 2.		Cell No. 3.		REMARKS.
			Temp. °C.	E. M. F. Volts.	Temp. °C.	E. M. F. Volts.	Temp. °C.	E. M. F. Volts.	
Start	1.00	14	50	0.48	53	0.48	46	0.50	
1	1.00	14	48	0.48	49	0.49	45	0.51	
2	1.10	15	48	0.49	49	0.49	43	0.51	
3	1.10	15	49	0.46	50	0.47	44	0.50	
4	1.10	15	48	0.47	50	0.46	42	0.48	Let run over night.
19	1.10	15	50	0.50	48	0.48	43	0.48	
24	1.10	15	47	0.48	49	0.48	42	0.48	Added 7 drops conc. HCl to each cell to clear solut.
30	1.15	16	47	0.48	55	0.52	45	0.50	Let run over night.
43	1.15	16	48	0.46	46	0.46	42	0.46	Added 6 drops conc. HCl to each cell.
47	1.15	16	47	0.46	49	0.47	43	0.48	
53	1.15	16	45	0.47	48	0.46	44	0.47	Let run over night.
67	1.12	16	48	0.46	51	0.46	46	0.48	Added 8 drops conc. HCl to each cell.
71	1.10	15	48	0.46	50	0.46	45	0.48	
77	1.10	15	44	0.49	50	0.47	45	0.48	Current off.

Weight of anode dissolved in Cell No. 3 was 89.78 grams = 99.92% current efficiency. The weight of iron deposited in Cell No. 3 was 83.87 grams = 93.45% current efficiency.

The low efficiency of the deposition was due to the electrolyte being slowly oxidized by exposure to the atmosphere, which produced ferric salts, and also to the addition of acid to the electrolyte, which caused the liberation of hydrogen, in place of an equivalent of iron, until the acid was neutralized. A precau-

tion which might have been taken in order to prevent this oxidation, is floating a layer of melted vaseline on the surface of the electrolyte, which was done formerly when I had occasion to produce absolutely pure lead for the determination of the electrochemical equivalent of lead in lead fluosilicate electrolyte.[12]

The addition of a few drops of conc. HCl to the electrolytes was made each day for the purpose of dissolving the basic salts, which was the result of atmospheric oxidation of the neutral electrolytes. When the acid was added, the turbid solutions became clear and gassing at the cathodes continued until the free acid was neutralized.

CONCLUSIONS.

Neutral ferrous fluosilicate electrolytes are not suitable for electrolytic refining of iron, as they are slowly decomposed with the separation of silica, which settles to the bottom of the cell and also collects in the anodes and cathodes.

The deposits from ferrous fluosilicate electrolytes are smooth and solid, of dull gray color and very brittle, due to the contained silica.

The E. M. F. required for electrolysis of ferrous fluosilicate electrolytes with a C. D. of 10 to 20 amperes per square foot, was 0.9 to 1.2 V. when temperature was 20 degrees C., and 0.55 to 0.70 V. when temperature was 60 degrees C.

Good deposits of iron were obtained by the electrolysis of neutral electrolytes containing either 8 per cent. of iron as $FeSO_4$, or 6 per cent. Fe and 3 per cent. Na as sulfates, or 8 per cent. Fe and 4 per cent. Na as chlorides.

The E. M. F. required for electrolysis of neutral $FeSO_4$ electrolytes containing about 8 per cent. Fe with a C. D. of 10 to 20 amperes per square foot, was 1.15 to 1.40 V., when the temperature was about 20 degrees C., and 0.80 to 0.98 V. when the temperature was about 50 degrees C.

The E. M. F. required for electrolysis of neutral sulfate electrolytes containing about 6 per cent. Fe and 3 per cent. Na, with a C. D. of 10 to 20 amperes per square foot was 0.95 to 1.20 V. when the temperature was about 20 degrees C., and 0.50 to 0.85 V., when the temperature was about 50 degrees C.

[12] Trans. Am. Elect. Chem. Soc., 6, 72 (1904).

The E. M. F. required for the electrolysis of neutral chloride electrolyte, containing about 8 percent. Fe. and 4 percent Na., with a C. D. of 10 to 20 amperes per square foot, was 0.6 to 0.8 V., when the temperature was about 20 degrees C., and 0.4 to 0.5 V., when the temperature was about 50 degrees C.

On starting the electrolysis of sulfate and chloride electrolytes, the deposits of iron peeled from the cathode and curled, due to the presence of ferric salts in the solution. After the solutions were electrolyzed for about three hours, the deposits formed smooth, solid and adherent.

Boiling the solutions previous to electrolysis liberated the dissolved gases, and caused the deposits to form less pitted.

The deposits of iron formed smoother when the electrolysis was conducted at 40 to 60 degrees C., than when conducted at normal temperature.

The deposits formed in neutral chloride electrolytes, containing iron and sodium chlorides, were finer grained and more flexible than those formed in neutral sulfate electrolytes.

The deposits of iron formed in neutral sulfate or chloride electrolytes, containing no ammonium salts, became quite malleable when they were heated above redness. The deposits from the chloride electrolytes, being finer grained, were the most ductile, and could be hammered double after being heated.

The deposits of iron from electrolytes containing ammonium salts were harder, more brittle, and also less rapidly oxidized than those from electrolytes which contained no ammonium salts. This suggested the possibility that iron formed in neutral ferrous-ammonium electrolytes contained either a nitride or an ammonium compound of iron.

When the electrolytes are not protected from the atmosphere, it is necessary to occasionally add a few drops of acid in order to clear the solution by dissolving the resulting basic salts.

When the electrolytes are not in use, they may be maintained in the ferrous condition by placing in stoppered bottles and adding a few pieces of wrought iron, either wire or strips.

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DISCUSSION.

Prof. J. W. Richards: I think it is opportune to emphasize the present opportunity for the commencement of an electrolytic iron refining industry. The production of fine grades of steel requires the highest quality of iron, free from sulphur and phosphorus. Steel is being sold at a price up to 75 cents per pound for the finer qualities of special steel. Under these conditions, the cost of the raw material is largely a secondary matter. The makers of these alloys could well afford to pay several cents a pound, if necessary, to get an absolutely pure iron which would introduce no possible impurity into their mixtures, and at the present time they do not use it, because it is not on the market. I believe there is a very clear field for the establishment of an electrolytic iron refinery which could put on the market and sell to the steel makers this electrolytically refined iron. Our worthy President and Dr. Kern and some others have worked faithfully on the subject and given us methods which I believe are open to any one to practice. Are they not?

President Burgess: Yes.

Prof. Richards: They have not been patented. The question simply calls for a little commercial enterprise in putting up the plant and making the product and selling it. I believe there will be an immediate market for this pure iron. It needs a little missionary work on our part, I think, to let the steel makers know of the metal, which is actually obtainable. If some one will simply put up the plant and put the material on the market, I am sure they will reap a large reward.

President Burgess: Allow me just a few remarks in connection with this paper. The deposition of iron electrolytically, electro-refining of iron, so-called, is successful from the laboratory standpoint. In commercializing it there will undoubtedly develop a number of problems which we have not encountered in the laboratory. The cost of refining should be low, fully as low as the cost of refining copper, and to those who may be interested in the commercial development of electrolytical processes for refining iron I would especially call attention to this paper which is before us.

Dr. Kern pointed out that the deposits from chloride solutions yield a satisfactory quality of iron, and in that respect his work is superior to my own, in that our work involved the use of ferrous-ammonium sulphate, and with his solution there can be no contamination or iron by nitrogen. Dr. Kern uses the chloride solution and avoids this contamination.

I would call attention to those performing experimental work on the deposition of iron that conclusions as to the quality of the deposits cannot be made in a few hours, or even in a few days, and that commercial electrolytically refined iron requires the production of rather thick cathodes; and a solution which will work satisfactorily for a few days, or even a week, at the end of two weeks is likely to give a great deal of trouble. That is the only respect in which I would offer any criticism to the work laid before us, I think the tests on the various electrolytes were not carried on long enough to show results desired.

In our laboratories we have been refining iron electrolytically steadily for three or four years, and as far as producing it continuously from the ferrous-ammonium sulphate solution, there is no question about its practicability.

Mr. A. W. Smith: I would inquire if it would not be a very easy matter to improve the product you have been making by the addition of vanadium, or some similar element?

President Burgess: I have no doubt it would be possible. Calcium would help, too. This material we are making is being used for alloys entirely, and work is being done along the line just suggested.

Mr. Anson G. Betts *(communicated)*: Dr. Kern has given us a valuable paper, of which one of the chief merits is the completeness of the data of solution-composition, current density and electromotive force. A publication of these important matters makes a welcome addition to the literature of the subject.

Mr. B. Starbuck has made some experiments in my laboratory, and afterward continued them himself, to find a good refining solution. Solutions were made up to contain in 400 c.c. 5, 10, 15, 20, and 25 grams NH_4Cl with respectively 95, 90, 85, 80 and 75 grams $FeSO_4 . 7H_2O$. The electrolysis was carried out at room temperature. The solution of 20 grams ammonium chloride and 80 grams hydrated ferrous-sulphate gave the best

deposit, and was thought to give the best general results. It continued in good working condition for as long as several weeks, and I see no reason why it should not have been good for an indefinite time.

Dr. Kern's results with ferrous-fluosilicate, it would seem, ought to be more in accord with the results he mentions getting with nickel fluosilicate. Very likely the preparation of the fluosilicic acid or the salts was different, and the nickel solution may have contained more fluoride than the iron solution. This is quite possible, as in preparing fluosilicic acid some HF is frequently left uncombined with silica. With an acid solution containing some fluoride, silica would be much less apt to form. There is probably no advantage to be derived by the use of iron fluosilicate, as the conductivity is only a little greater than that of a sulphate solution of equivalent strength, while the cost is much greater.

From Dr. Kern's figures, the following polarization voltages are arrived at:

Fluosilicate solution	21° C.	0.51 volt.
Fluosilicate solution	60° C.	0.21 "
Ferrous sulphate solution	47 °C.	0.28 "
Ferrous-sodium sulphate solution	47° C.	0.34 "
Chloride solution	47° C.	0.20 "

Edward F. Kern *(communicated)*: During the discussion of the paper, Mr. A. W. Smith inquired "if it would not be an easy matter to improve the product by the addition of vanadium or some similar element?" Prof. Burgess, in answer, said, "I have no doubt it would be possible. Calcium would help, too." This question and answer, I infer, have reference to the production of calcium-iron and vanadium-iron alloys, not in the electrolyzing cell, but by melting down the electrolytic iron and adding either calcium or vanadium. This, in all events, would be possible in the case of calcium-iron alloys, but for the production of vanadium-iron alloys, I question whether it could be done at the present time, as there is no method whereby pure metallic vanadium is produced. However, if Mr. Smith's inquiry was whether the addition of a salt of vanadium, or that of a similar element, to the iron electrolyte, would improve the product, I

would say it will not. In the case of vanadium, which stands below iron in the e. m. f. series, it would in all probabilities be precipitated, and an equivalent of iron take its place until no vanadium is left in solution, giving in the meantime a very unsatisfactory deposit if iron, intermixed with vanadium. The addition of a calcium salt to the electrolyte would probably act similarly to the presence of a sodium salt, as it stands above iron in the e. m. f. series.

Mr. Burgess seems to question the stability of the neutral iron-sodium chloride electrolyte, which was found to give the most satisfactory deposits of iron. He stated that "a solution which will work satisfactorily for a few days, or even a week, at the end of two weeks is likely to give a great deal of trouble." Since the paper was written, Mr. A. P. Frapwell, a graduate student in the department, produced deposits of iron which measured about ¾ inch thick, size 3¼ inches by 4 inches. He used the same chloride electrolytes which were used for the experiments given in the paper. Two cells were set up, using in each about 650 c.c. of electrolyte. One of the electrolytes (cell No. 1) was of same composition as original; it contained 8 percent. iron and 4 percent. sodium as chlorides. The other electrolyte (cell No. 2) was made to contain 8 percent. iron and 7 percent sodium, by the addition of a sufficient amount of sodium chloride. Before electrolyzing, both solutions were boiled for about two hours, in contact with sheet iron, in order to expel absorbed gases and to reduce ferric salts. The solutions were then diluted to their proper volumes with distilled water, and two wrought iron anodes and one sheet iron cathode placed in each cell. Surface of anodes exposed was 2½ inches by 4 inches (20 square inches). Surface of the cathodes exposed was 3 inches by 4 inches (24 square inches). The anodes were wrapped with two layers of washed muslin, so as to retain the anode sludge. After the electrodes were placed 1 inch apart in the cells, a layer of melted vaseline was poured on the surface of the electrolyte, for the purpose of preventing oxidation, and the subsequent formation of basic salts.

The electrolysis was conducted continuously day and night for almost three weeks, using a current density at the cathodes of about 15 amperes per square foot.

The average readings of cell No. 1, which contained 8 percent Fe and 4 percent Na, was 2.50 to 2.65 amperes, at an e. m. f. of 0.44 to 0.52 volts, and temperature of 45° to 67° C. (average 55° C.) The time of run was 16 days. Weight of deposit was 939.3 grams, thickness 11/16 inch.

The average readings of cell No. 2, which contained 8 percent Fe and 7 percent Na, was 2.50 to 2.65 amperes, at an e. m. f. of 0.42 to 0.54 volts, and temperature of 44° to 66° C. (average 55° C.). The time of the run was 19 days. Weight of deposit was 1,135.5 grams, thickness about 11/16 inch.

The cells were kept heated by being on sheets of asbestos on a hot plate. From time to time, during the day, the electrolytes were stirred.

The deposit from cell No. 1 was non-crystalline, very dense, but more nodular and more vertically ridged than the deposit from cell No. 2.

The deposit from cell No. 2 was non-crystalline, very dense and fairly smooth. It was less nodular and less vertically ridged than the deposit from cell No. 1. The presence of the larger amount of sodium chloride in the electrolyte retarded the formation of nodules and also prevented the vertical ridging of the deposit.

Two sets of anodes were used in each cell, one set lasting only nine days. When the second set was placed in the cells, the vaseline cover was removed, and the electrolytes then covered with a layer of engine petroleum oil, which proved to be a less satisfactory covering than the vaseline. When the oil was used, a larger amount of salts crystallized on the exposed tops of the electrodes, above the oil, and also the oil being of low specific gravity the electrolyte slowly evaporated, which was not the case when vaseline was used. (For our next runs, we intend using a layer of melted parafine to protect the electrolytes from oxidation, as it is a much cleaner material to handle.)

The electrolytes after these runs, were in as good condition as they were when used for the first set of experiments. The total length of time they were in use was almost a month, besides they stood in corked battles for over three months when not being electrolyzed.

The latter runs, made by Mr. Frapwell, show, without doubt, that neutral iron-sodium chloride electrolytes may be maintained

in good working condition for a long time. No trouble need be anticipated by their use, so long as they are protected from oxidation by a layer of vaseline or parafine, or else kept in working condition by the occasional addition of a few drops hydrochloric acid. The addition of hydrochloric acid has no detrimental effect other than cutting down the current efficiency for the time being, and the increase in iron content of the electrolyte, neither of which are of any great disadvantage.

Even when the electrolyte is protected by a layer of vaseline, some basic salts also form. In this case, it is necessary to add a few drops of hydrochloric acid every few days instead of every day, as was done when the electrolytes were exposed to the air.

Full experimental data of Mr. Frapwell's runs and that of other runs will be published later.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 1, 1908; President C. F. Burgess in the Chair.

ELECTRICAL TESTING OF IRON DURING THE ANNEALING.

By E. E. F. Creighton.

About five years ago, while engaged with the Stanley Electrical Mfg. Co., the problem of the annealing of iron was brought to the writer's attention. At this time, the company had the annealing done by the rolling mills, and considerable trouble was experienced with the variations in the permeability and core loss of the iron that was received, in spite of the utmost precautions taken in annealing. It is the object of this paper to describe the method used in studying the problem of annealing of iron for commercial use. The writer dropped the subject the following year, but, so far as known, the methods utilized at that time have not been described. The problem involved the study of the combination of electrical, chemical and physical conditions of the iron.

The problem relating to the annealing of the iron for electrical purposes involves the following subjects:

First, the chemical composition and process of manufactures.

Second, the proper treatment for bringing the hysteretic core loss down to a practical value.

Third, the treatment necessary to prevent the ageing of the iron after it is put into service.

The following discussion will be limited to the first two heads:

First, it is a well-known fact that two pieces of iron which have identically the same composition so far as ordinary chemical analysis can determine, may give entirely different values of core loss with identically the same methods of annealing; for example, a piece of sheet iron taken from a Bessemer furnace will invariably have a higher value of hysteresis than iron from the open-hearth process, in spite of all the ordinary methods of annealing. Incidentally, it would be interesting to compare the

iron produced by either of the foregoing methods with the iron from electro-chemical deposition. It is probable that the differences in the iron is due entirely to the absorption of gas

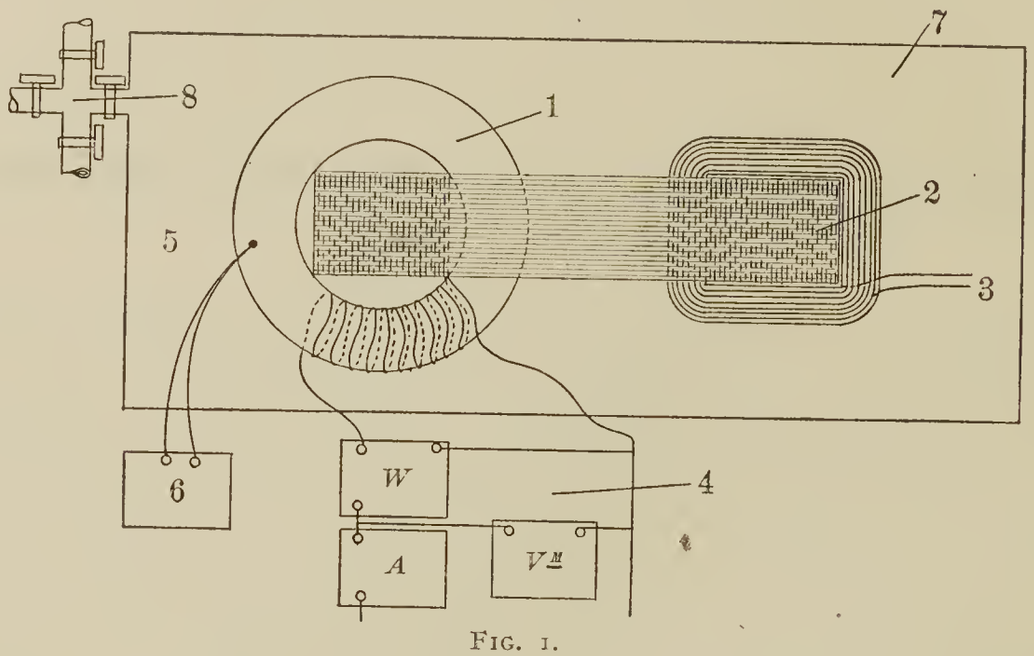


FIG. 1.

in one form or another. This will be referred to later in discussing results.

Second, the proper treatment of bringing the hysteretic core loss down to a practical value. To determine this treatment, a

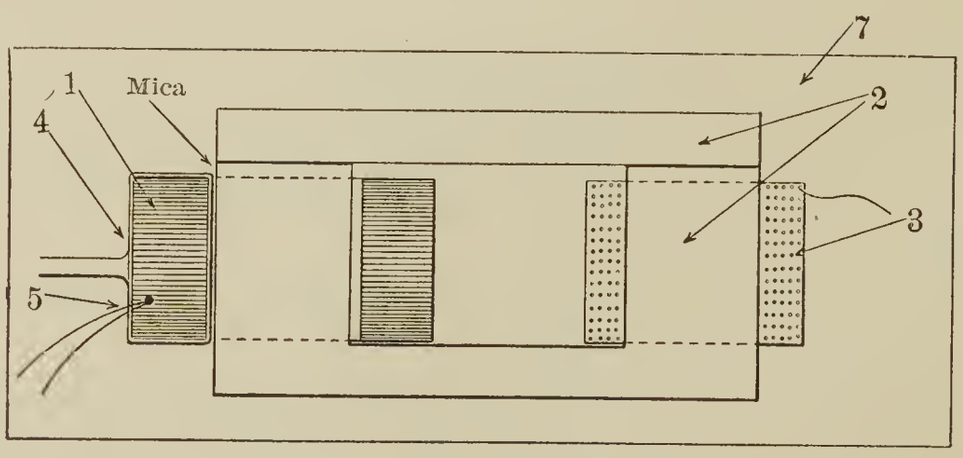


FIG. 2.

furnace was designed which permitted the measurements of the hysteresis and eddy currents for all values of temperature up to and down from the temperature where the iron becomes non-magnetic. This furnace was so arranged that the gas surrounding the iron could be chosen at will. Figs. 1 and 2 show dia-

grammatically the arrangement of the experimental furnace. The test piece of laminated iron is in the form of rings marked (1) in Fig. 1. These rings were stacked up to a height of about 2 inches. Through the center of these rings the iron core (2) of a transformer passes; this made the rings (1) the secondary of the transformer core which had (3) as primary winding. By impressing commercial frequency on the primary winding (3), the rings (1) could be heated to any desired temperature. The rings (1) were separated from each other by an inert powder, which prevented short-circuiting at high temperatures. Around this group of rings, a good quality of asbestos was laid, and over this asbestos was wound copper wire with asbestos insulation. This is shown in Fig. 1, as circuit marked (4). In the circuit (4) were the usual voltmeter, ammeter, and wattmeter, for making electrical measurements. Between the laminae at the point marked (5) a pyrometer was placed, which was connected to a galvanometer at point (6). In operating this apparatus, it was found necessary to disconnect the circuit (3) momentarily, while the electrical tests were being made on the test rings (1), as the circulation of the induced currents in (1) reduced the apparent core loss in (1); in other words, part of the core loss in the test piece (1) must have been carried by energy from circuit (3). In order to prevent the magnetic circuit (2) from acting as a short circuit to the test rings (1) while the tests were being made, a thin piece of mica was interposed in the magnetic circuit of the transformer core (2), at point (9) of Fig. 2. This small gap introduced a permissable reluctance in the magnetic circuit of the core (2), and yet rendered the iron acting as electrical circuit to the test rings entirely open. This apparatus was enclosed in an air-tight iron case, indicated by a broken line (7); the electrical leads were brought through air-tight joints in the base of this case. At the point (8) was connected a pipe, through which the gas in the furnace could be exhausted and replaced by any other gas in stock in the reservoirs.

The usual method of treatment was to begin with core loss measurements at room temperature and to take these measurements in steps up to the temperature of disappearance of magnetism. When the temperature approached red heat, the gas treat-

ment was begun. Various excess temperatures were employed and various rates of heating and cooling were tried. It was found that certain gases had marked effects on the iron if they came in contact with it during the time that the temperature

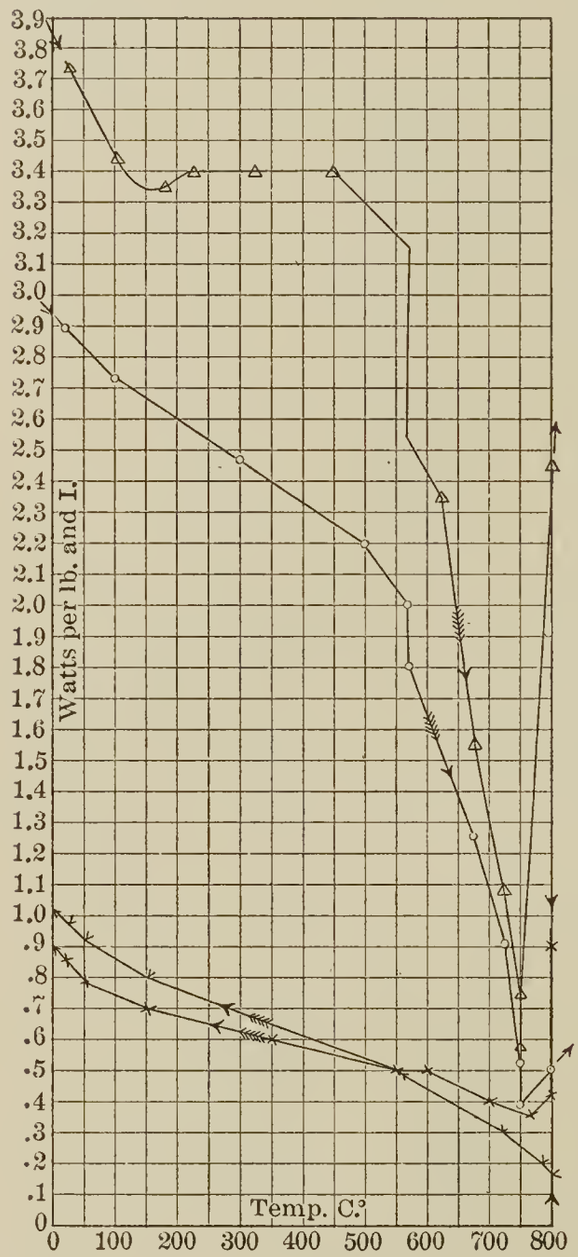


FIG. 3.

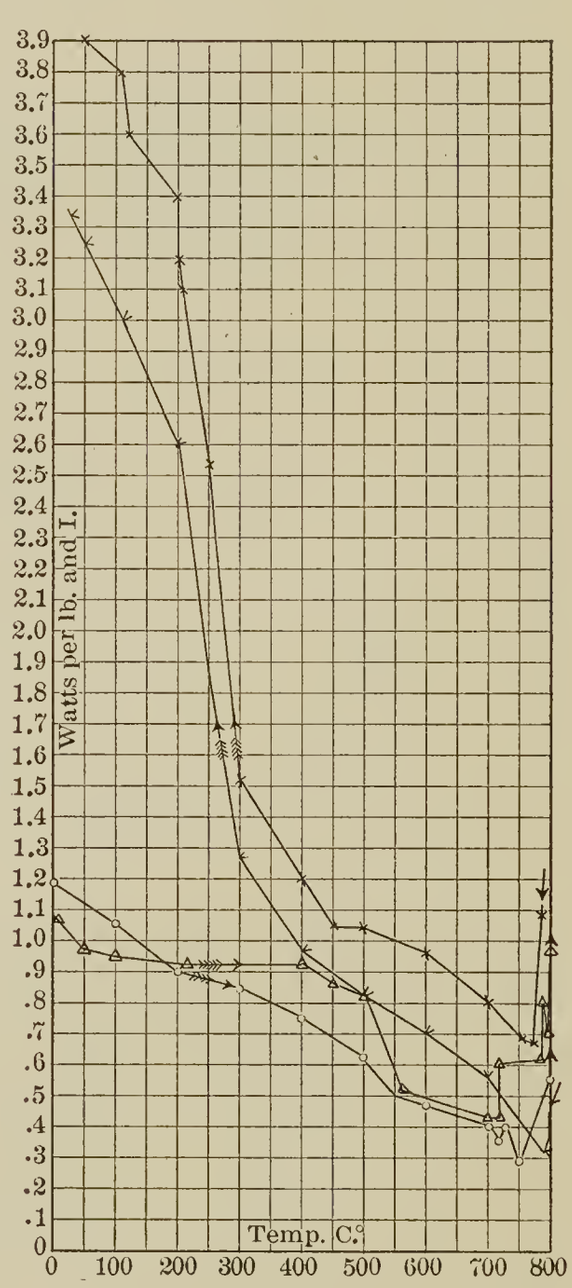


FIG. 4.

was above the temperature where the magnetism disappears. Some of the results are shown in the accompanied curves.

The curves shown in Fig. 3 and Fig. 4 are on the same test sample. Fig. 3 is the iron when first taken from rolling mill. The initial core loss was 2.9 watts per pound, and the corresponding exciting current 3.75 amperes. The temperature was caused to rise rapidly during the first seven tests up to 560° C.

The temperature was held constant during several minutes at 560°, and it will be seen that the annealing continued even at this comparatively low temperature. The core loss dropped from 2.0 watts to 1.8 watts, and the current from 3.18 amperes to 2.57 amperes. In the descending temperature curves, the core loss appears at .15 watt per pound, and gradually increases to 1 watt per pound at normal room temperature (some slight errors in plotting of the values of temperature are noted too late to correct before publishing).

During the second run on this sample, the iron was partially spoiled, so that the core loss rose to 1.18 from the previous value of 1 watt per pound. During the third annealing (Fig. 4), the iron was treated with ammonia gas, which ruined it entirely for electrical work. The core loss, on cooling, rose to 3.35 watts, which is ⅓ watt higher than the initial condition as it came from the cold rolls. The same treatment as previously used for recovering badly annealed iron was then applied, but without improving the core loss by any appreciable amount. From these tests and others, the conclusion is drawn that this iron has absorbed nitrogen gas and is in approximately the same condition as Bessemer iron.

DISCUSSION.

Mr. A. W. Smith: Was any attempt made to determine the chemical composition in the iron that had been heated in the ammonia?

Mr. Creighton: No attempt was made, but I have drawn my conclusions from the fact that I tried hydrogen gas, and it has not the same effect. The hydrogen gas in general has a beneficial effect upon the iron. I tried also pure nitrogen gas, and that had no detrimental effect.

Prof. J. W. Richards: A Swedish metallurgist, Braun, about two years ago, made an extensive investigation on nitrogen in steel, and he put nitrogen into the steel by passing ammonia over the hot steel. He analyzed the steel with different contents of nitrogen, and found marked effects on the elastic limit and tensile strength. He found 5 to 10 thousandths of a per cent. in crucible

steel, and from 10 to 20 thousandths of a per cent. in open hearth, and 20 to 30 thousandths of a per cent. in Bessemer steel, which corresponds with the known differences which you have spoken of.

Dr. C. P. Steinmetz: So-called chemically pure iron deposited electrolytically is not always soft iron, some samples of electrolytic iron showed extreme hardness and high hysteresis loss. The deposition was from iron ammonium sulphate, and this may account why the iron, which should be chemically pure, was as hard as steel: it really is not iron, but contains nitrogen or ammonia, etc. That would check with the observations of the paper.

President Burgess: A chemical analysis on electrolytically deposited iron shows the presence of nitrogen in its chemical composition in appreciable amounts.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 2, 1908; President C. F. Burgess in the Chair.

ELECTRIC FURNACE CONVERSION OF IRON PYRITES INTO A MAGNETIC FORM.

By O. L. Kowalke.

One of the important problems in preparing mixed sulphide zinc ores for the smelting operation is the removal of iron pyrites. A method commonly employed for removing the iron pyrites is first to convert the non-magnetic sulphide to a magnetic form by roasting the ore in a furnace where the products of combustion come in direct contact with the ore. After cooling, the roasted product is treated by a magnetic separator. In this roasting process some of the ore frequently becomes heated to an excessive temperature, and in the presence of oxidizing gases, red oxide of iron is formed which is non-magnetic. The purpose of the investigation described in this paper was to determine the temperature and the various atmospheric conditions under which iron pyrites can be made magnetic; also the loss of sulphur necessary for the attainment of this condition.

The Furnace.—A granular carbon resistance furnace proved to be the most feasible arrangement for heating the materials to the desired temperature.

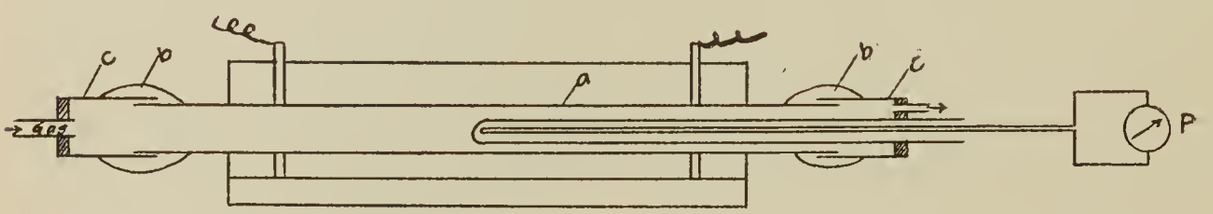
The furnace, whose inside dimensions were 3″ x 2½″ x 13″, was built of fire brick. A Royal Meissen porcelain tube (a) 26 inches long, one inch internal diameter and glazed on the inside served as the chamber in which the ore was treated. This tube, surrounded by the graphite resistor, lay lengthwise in the furnace. The furnace terminals were graphite slabs straddling the tube. To provide for suitable stoppers for the ends of the tube, glass sleeves (c) about 3 inches long, were slipped over the ends of the porcelain tube and cemented on by a mixture of magnesia and water glass (b). Besides providing for a stopper of sufficient size to admit the placing of inlet and outlet tubes;

these glass ends served also to prevent heat conduction from the porcelain to the stopper.

A thin layer of charred paper around the tube served to prevent any pitting action on the porcelain by the hot resistor particles even at temperatures above 1,000° C.

An alternating current at about 33 volts was sufficient to give the heat desired. The voltage, when applied to the furnace, brought the tube up to temperature quickly, and then by regulating the voltage, the temperature was maintained easily within 10° C. of the point desired.

Pyrometer.—A Le Chatelier platinum and platinum-rhodium couple standardized by the Reichsanstalt, and a Kaiser and Schmitt galvanometer served as an instrument for the measurement of the temperature. The pyrometer couple (P) Fig. 1,



encased in a porcelain tube projected through the stopper and extended to the middle of the heating chamber and touched the boat containing the ore.

Gas Generator.—A Kipp generator about 3 feet high served as a means of supplying the gas necessary for the various tests.

Electromagnet.—The electromagnet used was 2½ inches external diameter and 6 inches long. With a magnetizing current of 6.2 amperes, flowing in the winding, a flux was obtained sufficient to hold up 4,830 grams of soft iron.

Procedure of Tests.—In all cases the material used was pure marcasite. This was crushed and sized, and that portion which passed a 20 mesh sieve and caught on a 40 mesh was used for the tests. The weight of marcasite for each test was determined on an analytical balance, then the charge was placed in a porcelain boat 2″ x 3/16″ deep x ¼″ wide and put into the furnace. After sealing the furnace the gas in which the ore was to be tested was passed through for at least 20 minutes to insure complete expulsion of air before the current was applied. The

surface was heated slowly to insure an even distribution of heat; this usually took an hour or more. When the desired temperature was attained it was kept at that value within about 10° C. by regulating current and voltage on the furnace. After the ore had been treated a sufficient length of time the current was cut off, but the gas allowed to pass through the tube until the temperature had fallen to at least 180° C. before the tube was opened. The ore was then removed and tested under the magnet for magnetic qualities. In all cases the magnetizing current was kept close to 6.2 amperes. The magnetic and non-magnetic portions were again carefully weighed.

In computing the percentage of magnetic portions the amount taken from the furnace served as a basis. The percentage loss is based on the amount taken for the test.

Tests in Air.—The procedure varied somewhat in this test from the general scheme—the heating tube was open to the air at one end and the ore was roasted in a closed cylinder to avoid too much exposure to oxidation. A cylinder of iron 3/8″ diameter and 1″ long, closed at both ends with the exception of a small hole to allow the escape of fumes, proved unsatisfactory. The sulphur vapors which were driven off attacked the iron and a fluxing action between the iron and ore took place so that it became impossible to account for losses. A porcelain cylinder of the above size whose ends were closed by stoppers each with holes of 1/32″ in diameter gave the best results. Thus an atmosphere composed of sulphur vapors and air was attained.

The furnace was first brought up to temperature and then the charged cylinder put in the tube. After heating the cylinder and charge this was taken out into the air and left to cool. When cool the separation tests were made with the magnet. The magnetic portion varied in color from a black to blue-black, while the non-magnetic residue was yellow.

The results of tests 1 to 10 in Table I will be omitted, as the loss could not be determined, and hence only the results of tests in a porcelain cylinder will be given.

Tests Under Reduced Pressure.—In this series of tests an open porcelain boat, as before described, held the ore. After placing the ore in the furnace, all openings were securely closed and an

aspirator bottle attached. The pressure was reduced about 55 m.m. of mercury, when the furnace was cold, and about 45 m.m. when hot, for at the high temperature the leaks were somewhat larger.

TABLE I.

No. of Test.	Kind of Material	Grams Taken.	Time in Minutes.	Range of Temperature in Degrees C.	Grams Magnetic.	Grams Non-magnetic.	Grams Total Taken from Furnace.	Per cent. Magnetic.	Grams Lost.	Per cent. Loss.	Remarks.
11	Marcasite	1 8155	45	669-674	1.0400	0.6405	1.6805	60.47	0.1350	7.43	Porcelain boat.
12	"	2.1030	60	679-679	1.2305	9.6785	1.9090	64.45	0.1940	9.22	
13	"	1.6380	120	677 680	1.2525	0.0745	1.3270	94.38	0.3110	18.48	Rolled boat.
14	"	1.2665	120	703 705	1.0445	0.0115	1.0560	98.91	0.2105	16.62	

Table II shows the results, and it is interesting to note that the ore becomes magnetic at 150° C. lower than under atmospheric pressure and in half the time.

The appearance of the roasted ore particles was a bluish black. Only the outside layer of the particles had changed color, for the inside was yellow and apparently unaffected. Run No. 37

TABLE II.

No. of Test.	Kind of Material	Grams Taken.	Time in Minutes.	Range of Temperature in Degrees C.	Grams Magnetic.	Grams Non-magnetic.	Grams Total Taken from Furnace.	Per cent. Magnetic.	Grams Lost.	Per cent. Loss.	Remarks.
36	Marcasite	1.2725	60	579-592	1.1775	0.0000	1.1755	100.00	0.0970	7.62	
37	"	1.2725	60	542-554	1.1633	0.0000	1.1633	100.00	0.1092	8.58	Best Vacuum.
38	"	1.2725	60	477-492	1.1705	0.0180	1.1885	98.48	0.0840	6.67	

was made under the best vacuum and here a loss of only 8.58 per cent. is shown.

Tests in Hydrogen.—The hydrogen for the tests was made in a Kipp generator from electrolytic iron and hydrochloric acid. From the generator the gas passed successively through wash bottles containing solutions of potassium hydrate, potassium per-

manganate, potassium pyrogallate, concentrated sulphuric acid, and fused calcium chloride, then through the furnace over the ore and finally through a bottle containing lead acetate acidified with acetic acid. Before the heating current was turned on, hydrogen passed through the above train for at least 20 minutes.

At a temperature of 494° C. in the furnace a black precipitate appeared in the lead acetate bottle. The precipitate increased in volume with an increase in temperature, so that at 507° C. the precipitate was formed in large amounts. In run No. 18 the test was allowed to proceed at a temperature between 503° and 522° C. until no more precipitate appeared in a fresh bottle of lead acetate. In this run there was a loss of only 2.93 per cent

TABLE III.

No. of Test.	Kind of Material	Grams Taken.	Time in Minutes.	Range of Temperature in Degrees C.	Grams Magnetic.	Grams Non-magnetic.	Grams Total Taken from Furnace.	Per cent. Magnetic.	Grams Lost.	Per cent. Loss.	Remarks.
15	Marcasite	1.2915	30	584-632	0.8550	0.1030	0.9580	89.40	0.3335	25.80	Put in boat at 507° C.
16	"	1.3425	160	508 657	0.9910	0.0205	1.0115	97.97	0.3510	32.92	Couple parted.
17	"	0.9905	928	494-1172	0.6365	0.0000	0.6365	100.00	0.3540	35.74	Hydrogen gone at 1172° C.
18	"	0.9710	100	503 522	0.9410	0.0015	0.9425	99.85	0.0285	2.93	

The resultant grains were blue-black in color, due to a thin magnetic layer, for the inside was still yellow. It takes heat, evidently, to crack the particles of ore open so that the hydrogen can get at the inner portions, for an increase in the temperature produces a further formation of lead sulphide in the bottle of lead acetate. To see how high a temperature would have to be attained beyond which no more hydrogen sulphide is given off, the product of Run No. 16 was used for No. 17 and heated to 1,172° C. At this point the supply of hydrogen gave out and the precipitate was still being formed. The product was a metallic appearing mass which was highly magnetic. In iron pyrites there is 46.6 per cent. iron, and the iron content in the amount taken for Run No. 16 is 0.6254 grams. The residue in

No. 17 weighed 0.6365 grams, hence the resultant product was within 1 per cent. of being metallic iron.

It is interesting to observe that hydrogen reduces marcasite to a magnetic sulphide at the low temperature of 494° C., and further, that hydrogen suphide seems to exist at the high temperature of 1,172° C. Meyers, in Annalen der Chemie, 159, p. 124, claims that hydrogen sulphide is decomposed at 400° C., while on the other hand, Watt's Chemical Dictionary claims that hydrogen sulphide is formed from hydrogen and sulphur vapors at 400° C.

Tests in Carbon Dioxide.—Carbon dioxide gas was generated in a Kipp generator from marble and hydrochloric acid, and before being used in the furnace was washed in the following train: water, silver sulphate solution, concentrated sulphuric acid and calcium chloride. The air in the entire train was displaced by carbon dioxide before heating was begun.

At about 507° C. free sulphur vapors appeared and at 567° C. an odor of sulphur dioxide was detected. In Run No. 39, three liters of gas coming through the furnace at 592° was passed successively through two bottles each containing 15 c.c. of 1/10 N. iodine solution. The excess of iodine was titrated with sodium thiosulphate and it appeared that 5.95 c.c. of sulphur dioxide had formed. It might seem that the following reaction took place: $x\ FeS_2 + 2\ CO_2 = Fe\ x\ Sy + 2\ COS + SO_2$, but since no test for COS could be obtained the explanation does not appear to be a sound one. No test was made for free oxygen in the incoming gas. It is probable that there was a little oxygen in the pores of the marble, and since no provision was made for the removal of oxygen, the small amount of sulphur dioxide probably was formed from the free sulphur and this oxygen.

In comparing the results of these tests as shown in Table IV, it is seen that the loss is variable at temperatures that do not differ so widely. It is seen that a magnetic product can be attained as in run No. 34 with a loss of only 7.76 per cent.

Tests in Carbon Monoxide.—Carbon monoxide was generated by passing carbon dioxide over charcoal heated to redness. Before feeding the gas into the furnace it was purified in a train consisting of two bottles of saturated solution potassium hydrate, a bottle of saturated solution of barium hydrate, and some calcium chloride.

The ore and furnace were prepared in the usual manner. The gas after having passed through the furnace was bubbled through a column of distilled water. According to Watt's Chemical Dictionary carbon monoxide and sulphur combine: $CO + S = COS$, and the product again decomposes in water: $COS + H_2O = CO_2 + H_2S$. These reactions were found to take place. At the end of a run after the waste products had bubbled through the bottle of water during the entire test, the bottle was stoppered and set aside over night. In the morning a

TABLE IV.

No. of Test.	Kind of Material	Grams Taken.	Time in Minutes.	Range of Temperature in Degrees C.	Grams Magnetic.	Grams Non-magnetic.	Grams Total Taken from Furnace.	Per cent. Magnetic.	Grams Lost.	Per cent. Loss.	Remarks.
19	Marcasite	1.1670	60	479-494	0.4415	0.7075	1.1490	47.28	0.0180	1.54	
20	"	1.5250	60	579-602	1.2495	0.1085	1.3580	92.01	0.1670	10.95	
21	"	1.4725	60	592-595	1.1612	0.1843	1.3455	86.30	0.1270	8.61	Tested for SO_2.
22	"	1.4445	60	650-655	1.1175	0.0000	1.1175	100.00	0.3270	22.65	SO_2 estimated.
23	"	. . .	. .	. .	. . .	. . .		. .	. . .		Couple parted.
24	"	1.6905	60	622-632	1.2235	0.0190	1.2425	98.43	0.4480	26.50	Iron pyro. tube.
25	"	1.7030	60	622-632	1.3272	0.0045	1.3317	99.67	0.3713	21.75	" " "
26	"	1.3505	60	614-624	1.0960	0.0000	1.0960	100.00	0.2545	18.85	Porc. " "
27	"	1.5495	60	514-524	0.8000	0.6905	1.4905	53.67	0.0490	3.19	
28	"	1.2890	60	579-602	1.1865	0.0065	1.1950	99.28	0.0960	7.44	
29	"	1.3065	60	542-550	0.9595	0.2825	1.2420	77.25	0.0645	4.93	
30	"	1.2678	60	587-607	1.1190	0.0025	1.1215	99.78	0.1463	11.54	
31	"	1.3889	90	582-602	1.2155	0.0000	1.2155	100.00	0.1734	12.48	Slow stream CO_2.
32	"	1.2405	90	591-594	1.0328	0.0000	1.0328	100.00	0.2077	16.74	CO_2 shut off at
33	"	1.3362	25	562-567	0.2660	1.0510	1.3170	20.19	0.0912	1.43	400° C.
34	"	1.4455	90	592-592	1.3325	0.0007	1.3332	99.94	0.1123	7.76	Rapid stream CO_2
35	"	1.5595	30	567-567	0.3380	1.1915	1.5295	22.12	0.0300	1.92	" " "
39	"	1.2725	60	590-609	1.0428	0.1025	1.1453	91.00	0.1272	10.00	Took sample Gas.
40	"	1.2725	30	704-712	0.9640	0.0000	0.9640	100.00	0.3085	24.24	

distinct test for H_2S was obtained by holding a paper moistened with lead acetate at the exit of the bottle as the gas in it was displaced.

Table V shows the marcasite can be made magnetic in an atmosphere of carbon monoxide at a temperature about 80° C. lower than in carbon dioxide. The loss in Run 43 is only 11.70 per cent. The product from Runs 41 and 42 was black, soft and homogeneous. The large loss in Run 42 in the short period of time seems to indicate that FeS_2 can also be reduced to metallic iron by carbon monoxide.

TABLE V.

No. of Test.	Kind of Material	Grams Taken.	Time in Minutes.	Range of Temperature in Degrees C.	Grams Magnetic.	Grams Non-magnetic.	Grams Total Taken from Furnace.	Per cent. Magnetic.	Grams Lost.	Per cent. Loss.	Remarks.
41	Marcasite	1.2725	60	547-547	0.9552	0.0000	0 9552	100.00	0.3173	24.93	
42	"	1.2725	30	592-592	0.9468	0.0000	0.9468	100.00	0.3257	25.60	
43	"	1.2725	60	507-517	1.1172	0.0065	1.1237	99.41	0.1488	11.70	

Temperature at Which Sulphur is Given Off.—The tests on marcasite heated in air and sulphur vapors did not permit the determination of the temperature at which sulphur begins to distill. A special muffle and condenser of graphite was prepared. A cavity 4″ x 4½″ x 8″ was machined out of a graphite block and a cover fitted. A cylindrical condenser 3½″ x 8″ communicated with the cavity by a one inch round passage way 2½ inches long. A hole in the side of the graphite block or muffle served as a receptacle for a pyrometer. The muffle was packed in a granular carbon resistor to be heated, and the condenser was outside the furnace walls. Pure marcasite was heated in the muffle and the temperature observed at which sulphur appeared in the passage from the muffle to condenser. The following is a log of this determination:

Time.	Temp.	Remarks.
9:08	22° C.	Started.
9:26	382 "	Faint crackling in muffle.
9:35	512 "	Odor of SO_2 appeared.
9:40	582 "	Sulphur vapors visible at opening into muffle.
9:43	612 "	" " coming freely. S. flame maintained
9:48	662 "	" " " "
10:10	697 "	" " stream getting smaller.
10:20	682 "	" " " almost ceased.
10:25	702 "	" " " coming rapidly again.
10:30	732 "	" " " still " "
10:45	732 "	" " " " slowly.
10:53	752 "	" " " " more rapidly.
11:00	762 "	" " " just visible.
11:18	822 "	" " " increased, but soon stopped
11:27	826 "	" " white.
11:45	832 "	" burning in small flame in condenser.
12:18	872 "	No vapors of sulphur and no flame—stopped.

Run No. 50.—Put 700 grams of marcasite crushed to about a 6-inch mesh in the muffle and heated.

The residue was soft, blue-black in color, wholly magnetic and not sintered. The weight of the product was 546 grams, thus showing a loss of 154 grams, or 22 per cent. This loss agrees very well with Run No. 40, where the loss is 24.2 per cent. at a slightly lower temperature.

CONCLUSIONS.

The following conclusions may be drawn from these tests:

1. That it is not necessary to roast pyrite or marcasite to a homogeneous mass in order to obtain a magnetic product. A loss of sulphur of from 3 to 12 per cent. is sufficient to produce a coating, such that its magnetic properties will cause the whole particle to be picked up.

2. Roasting in a reducing atmosphere and under a slightly reduced pressure requires a lower temperature than in a neutral atmosphere, and causes a smaller loss of sulphur to form a magnetic product.

3. That, in a neutral atmosphere, sulphur begins to distil from FeS_2 at about 510° C. and continues to come off up to about 680° C. The roasting could be stopped slightly above 600° C., as shown by tests 31 and 34, providing the atmosphere is neutral. If the temperature is increased beyond 680° C., the sulphur is driven off until FeS results.

4. Marcasite can be reduced to a metallic iron in an atmosphere of hydrogen.

In conclusion the author wishes to express his appreciation to Prof. C. F. Burgess and Prof. O. W. Brown for the many helpful suggestions and the criticisms they made during the progress of the work.

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THE ALLOYING OF CALCIUM AND IRON.

By Alcan Hirsch and James Aston.

While attempting to prepare pyrophoric alloys of cerium and iron by reducing the oxides of the metals with metallic calcium, it was observed that the metallic masses obtained very often contained calcium as well as cerium and iron. In some few cases iron and calcium only were found by qualitative tests to be present in lumps which were easily oxidized in the air. The recurrence of these intimate mixtures of iron, calcium and cerium led the writers to an investigation of the possibility of alloying the first two metals, in the absence of cerium, which was thought at first to influence the reaction. This work was done incidental to a line of research now being carried on in the Laboratories of Applied Electrochemistry of the University of Wisconsin, under a grant of the Carnegie Institution to Prof. C. F. Burgess.

The literature on the subject is not only very meagre but is also in many cases directly contradictory. Howe, in his Metallurgy of Steel, page 89, says that it is uncertain whether calcium can be alloyed with iron, but quotes from other references, namely: A spiegel of 0.091 per cent. Ca and several cast irons of 0.02 to 0.46 per cent. Ca, by Karl[1]; a wrought iron of 0.1774 per cent. Ca, by Karsten[2], which was deficient in welding and tenacity but neither red nor cold short. Percy[3] quotes, but doubts, a cast iron of 1.37 per cent. Ca. J. W. Gray[4] finds from 0.79 to 14.40 per cent. Ca in high grade electric furnace ferro-silicon, and Ledebur[5] in following up this point, because of its contradiction, to the more common belief that calcium and iron form no alloys,

[1]Grundriss der Eisenhuttenkunde, p. 42.
[2]Percy, Iron and Steel, p. 197.
[3]Percy, Iron and Steel, p. 542.
[4]Journal Iron and Steel Institute 1901, Part II, 144.
[5] Ledebur, Stahl und Eisen, 22, 710.

is unable to introduce calcium into steel, but confirms Gray's results as regards ferro-silicon, and contends that calcium will alloy with iron only in the presence of silicon at electric furnace temperatures. C. Quasebart[6], in an extended and varied series of trials, concludes that calcium will not alloy with iron whether the latter contains carbon or not. On the other hand, L. Stockem[7] says that calcium dissolves in molten cast iron with great development of heat, but when large quantities are used the metal is rapidly coated with a crust of calcium carbide which prevents further action, and some calcium carbide always remains mechanically entangled in the iron. He finds also that ferric oxide and excess of calcium gives a very vigorous reaction but without the formation of an alloy. Watts[8] also finds entirely negative results.

It was thought at first that the successful alloying of calcium and iron would depend upon the presence of a third metal, such as cerium, but, owing to the scarcity of cerium oxide on hand at the time, it became necessary to select another metal which it seemed likely would effect the alloying. Because of the readiness with which copper and iron alloy, it seemed possible that copper might be the agent required. The charge of calcium-copper alloy and electrolytic iron was placed in a medium-sized (3″ diameter) magnesia crucible. A thick layer of powdered magnesia was placed on top of the charge in the magnesia crucible to prevent oxidation. The magnesia crucible was then slipped inside a graphite crucible and heated in a resistor furnace for a length of time which experience has taught is sufficient to completely fuse a 400 gram iron charge in that size furnace and with the available energy. Some fumes were evolved during the heating, and after cooling, a homogeneous ingot was obtained, but entirely free from calcium. Unless otherwise stated the above method was employed in all fusion experiments. The covering of powdered magnesia has proved to be an excellent preventative against oxidation. On being heated it fuses together slightly but allows all vapor to escape freely.

It was hoped that by heating hematite (Fe_2O_3) with the requisite amount of calcium carbide, carbon dioxide and an iron-

[6]C. Quasebart, Metallurgie, 3, 28, (1906).

[7]Stockem, Metallurgie, 3, 147, (1906).

[8]Watts, J. Am. Chem. Soc., Sept., 1906.

calcium alloy would be formed. However, the products of this reaction were lime and iron similar to pig iron.

If electrolytic iron and metallic calcium are heated together in the electric furnace, on cooling, the ingot is free from calcium. If the crucible is well imbedded in the furnace practically no lime nor calcium is found on the walls of the lining nor on the cover, both of which are intact. In nearly every case where calcium was heated to the melting point of pure iron—1,500°C—some fumes were noticeable above the crucible top. The only explanation for the complete disappearance of the calcium is that it was volatilized.

The writers were not convinced that there is no alloying tendency of iron and calcium simply because on heating calcium and iron the resulting ingot contains no calcium. It was decided that failure to alloy these metals could only be logically acknowledged when, after fusion and subsequent cooling, the two metals are found segregated and unalloyed.

In order to prevent the calcium from escaping before the iron was fused, a charge of electrolytic iron was melted and a lump of calcium securely fastened to the end of an iron rod quickly plunged into the molten mass. A violent reaction occurred. Showers of sparks were emitted and it was impossible to cover quickly with powdered magnesia. No calcium was found in the iron.

One fruitless attempt was made to introduce calcium into molten iron containing silicon.

It was purely accidental that a good proof was obtained of at least one of the important reasons why it is impossible to alloy iron and calcium by heating them to or above the melting point of pure iron. Owing to the fact that an almost explosive reaction occurs when calcium is introduced into molten iron, the calcium was placed in a thin wrought iron case, closed at each end by thin cast iron caps. The calcium was shaped so as to very closely fit the interior of the case and weighed 37.2 gm. The empty case and caps weighed 138 gm. Four hundred gm. electrolytic iron was thoroughly melted and the plug shoved, as far as possible, beneath the surface and quickly covered with powdered magnesia. The heating current was immediately shut off, and after a few minutes the crucible was removed from the fur-

nace. After cooling, the ingot was sawed in two longitudinally, a photograph of one section being herewith shown.

The top cap and the case are intact, but the bottom cap is fused. There are large blow-holes showing the manner in which the calcium made its escape. Here, then, was a reasonable proof of the cause of failure to get alloys under ordinary fusion conditions. At the melting temperature of the iron, the calcium had volatilized, and the increased pressure had forced the vapor downwards and outwards through the molten iron. When this pressure diminished and the iron cooled, the remaining calcium was held. The body of the ingot contained 0.14 per cent. Ca but a thin shell between the blow-hole and the interior of the plug,

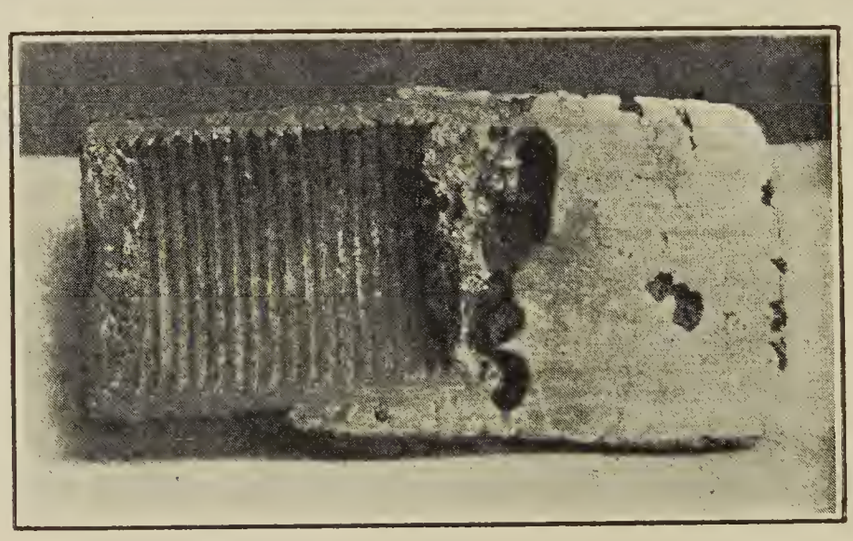

Fig. 1.

and through which the escaping calcium had passed, contained by analysis Ca 6.75 per cent., Fe 93.1 per cent.; total 99.85 per cent. The theoretical amount introduced was 6.9 per cent.

The above experiment was repeated, except that the case and caps weighed 189.4 gm., the electrolytic iron 400 gm. and the calcium 38 gms. The theoretical per cent. of calcium introduced was 6.45 per cent. The case was completely immersed below the surface of the molten iron and although the current was immediately shut off, the crucible was allowed to cool in the furnace. The melt was good, but that the fusion was hardly complete was shown by the fact that the ingot was rather cone-shaped on top. When sawed longitudinally through the center it appeared very homogeneous, although there were some blow-holes in the interior. The percentage of calcium present was 0.2 per cent.

Upon heating these two ingots to ordinary forging temperature disintegration set in, and a blow with a steam hammer caused the metal to crumble; as the temperature decreased, however, it was possible to forge to thin sections, but impossible to weld the disintegrated part. Qualitative tests of the sample after forging still indicated the presence of Ca.

These latter experiments indicated that the vaporization of the calcium was a very important factor in the preparation of these alloys, and a determination of the vaporization point of calcium, described at the end of this paper, was subsequently made.

In order to prevent the escape of the calcium it was determined to reduce Fe_3O_4 with excess of calcium under pressure. It was found that calcium cut on the milling machine into fine shavings was very suitable for this work. The top of the charge was covered with a little sodium peroxide and calcium filings intimately mixed, and lastly with some powdered magnesia. The crucible containing the charge was placed in the firing cylinder consisting of a magnesia lined steel shell bolted between two heavy steel flanges, the top was bolted on, and the charge fired electrically. The size of the cylinder was such that only comparatively small melts of iron could be obtained, yet the results were uniformly successful. In every case the iron and the calcium formed homogeneous mixtures, and although in some instances many lumps were found scattered all over the interior of the crucible, owing to the vigorous reaction, yet in no case did segregation of the iron and calcium occur; they were always found together. A likely explanation is that the increased pressure raised the vaporization point of the calcium sufficiently to keep it in the liquid state whereupon it alloyed with the iron.

In most cases a fairly large excess of calcium was used. The lumps of metallic iron always contained calcium in small amounts. In several instances there were obtained pieces of metal resembling calcium and very readily oxidized by exposure to the air. They were homogeneous, but always contained iron. An analysis of one gave 52.5 per cent. Ca. Doubtless the reduction of the Fe_3O_4 occurred in a large excess of calcium and owing to the rapid cooling the iron was mechanically held in the calcium.

The following alloys were prepared by this "thermit" method. The analyses are of the homogenous iron particles:

Lab. No.	Charge.			Weight Resulting Alloy.	Per Cent. Ca.	Remarks.
	Calcium.		Fe_3O_4			
	Shavings.	Lump.		Grams.		
165 I	30	30	44	13	1.37	Some white lime and considerable black slag were obtained. Alloy was in lumps. Slowly evolved H in water. No test for C_2H_2 with ammoniacal cuprous chloride.
165 M	46	26	68	60	0.6	Complete reaction. Some slag.
165 N	50	10	66	10	0.29	Good melt. Alloy soft and tough. Fibrous fracture.

In the above alloys some of the calcium undoubtedly was present in the slag. In every case tests were made to find if any calcium was segregated from the iron, but where one metal was present the other was also found.

The alloys above .5 per cent. Ca will evolve gas from hot water and No. 165 I. will slowly decompose water in the cold. It may be well to state here that special precautions were taken in the analysis. The samples were always thoroughly cleaned, and if gas evolved when the samples were put in hot water it was tested for C_2H_2 with ammoniacal cuprous chloride; in all cases acetylene was absent. The iron was precipitated as hydroxide, filtered and washed, and the calcium precipitated as oxalate with ammonium oxalate filtered on a fine Swedish filter paper and washed thoroughly with hot water, dissolved in hot diluted H_2SO_4 and titrated with standard $KMnO_4$. Owing to the fact that only a few c. c. of $KMnO_4$ were required for the small amount of Ca present, a blank was run as follows: A solution of ammonium oxalate was filtered through a clean Swedish filter paper which was thoroughly washed with hot water. Hot dilute H_2SO_4 was run through the filter paper and collected in a small Erlanmeyer flask. One twentieth c. c. $KMnO_4$ was sufficient to give a pink color to the solution.

As a result of these experiments the following conclusions may be drawn:

(1) That failure in alloying Ca and iron is not due to any inherent disinclination on the part of the metals themselves to

alloy, but is dependent mainly on the tendency of the calcium to volatilize at the melting point of iron. The result could probably be obtained in a furnace where the contents of the crucible could be kept under sufficient pressure.

(2) That there is very little likelihood of any success in alloying Ca and Fe under ordinary conditions or of finding Ca in iron made by ordinary metallurgical processes.

(3) That the presence of calcium in iron in even very small amounts destroys the welding qualities of the material. Alloys above 4 per cent. Ca oxidize very readily in the air.

THE VAPORIZATION POINT OF CALCIUM.

To check the vaporization point of Ca, which the above experiments indicated as being below the melting point of iron, a separate test was made for this purpose. A large lump (60 gm.) of Ca was placed at the bottom of a magnesia crucible. Fitting inside the crucible, and resting upon the lump of Ca was a magnesia partition with a hole ½″ diam. in the center. This was to prevent spattering of the Ca and to allow the vapors to pass upwards into the chamber above, through the hole. The magnesia crucible was placed inside a graphite jacket, and a graphite cover screwed into the latter. Through the cover of the jacket were two holes; in the center one was a thermo-electric couple with its junction just above the hole in the magnesia partition; the other hole was for the escape of the Ca vapors.

The whole apparatus was placed in a resistor furnace and gradually heated to a maximum temperature of 1380°. With the current cut off, the temperature fell gradually to 1290°, and there remained constant for several seconds, then fell gradually to 1100°. At this point, the heat was again increased, and, as in the previous heating, when a temperature of 1280° was reached, a yellow flame appeared at the outlet, and increased in intensity as the temperature arose to a maximum of 1360°. In cooling, the flame ceased at about 1300°, but no halt in the temperature drop was noted, probably due to the fact that there was very little Ca left in the crucible.

After the crucible had cooled, an examination showed that all of the calcium had disappeared. About 5 gm. of a white sub-

stance, seemingly calcium oxide, was inside the crucible. At the hole in the cover, there was a small amount of calcium nitride. The only plausible explanation for the disappearance of the calcium seems to be that it had volatilized.

This experiment seemed to indicate a vaporization point of the Ca at about 1290° C., or well below the melting point of iron.

Laboratory of Applied Electrochemistry,
University of Wisconsin,
April 8, 1908.

DISCUSSION.

Prof. J. W. Richards: I think it might be possible to obtain the iron alloys from the calcium zinc alloy, which latter alloy combines quite readily with iron, and from which the zinc can be volatilized at lower temperature than the calcium, the boiling point of zinc being only 930.

President Burgess: Alloys of calcium and zinc were made, and I doubt whether you can volatilize all the zinc out of iron without melting the iron, in which case you would get temperature high enough to volatilize the calcium as well.

Prof. Richards: You say that 1,290 to 1,300 degrees is the temperature at which the calcium volatilizes, and is the boiling point. Did you mean boiling point at atmospheric pressure?

President Burgess: Yes.

Prof. Richards: There is a great confusion concerning the question of boiling points of the metals. Some have a volatilizing point which is very low. That is a point at which they have some perceptible vapor tension, and volatilize. There is apt to be confusion as to what the boiling points are. I would like to know, definitely, whether 1,290 degrees to 1,300 degrees is the boiling point under atmospheric pressure, or at some partial pressure.

President Burgess: The paper describes what the authors mean by the boiling point. It is the temperature at which the calcium escapes very rapidly from the crucible or containing vessel, and it is indicated by the constant reading of the pyrometer, while that particular act is taking place.

PROF. RICHARDS: In the case of the calcium and zinc alloys, will not the zinc boil away from the calcium alloy at a different temperature from what zinc will boil itself, since the fact that the two are alloyed has an effect on the temperature, at which one volatilizes, just the same as the boiling of water from a salt solution?

MR. A. HIRSCH: We do not claim having determined the boiling point of calcium. It has simply been found that under atmospheric pressure calcium volatilizes at about 1,300° C. It seems reasonable to suppose that if calcium alone volatilizes at a temperture about 200° below the melting point of pure iron, and as there seems to be no great alloying affinity between the two metals, that if calcium be added to molten iron, unless a rapid cooling is effected, the resulting ingot will contain no calcium. This has been corroborated by experiment.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 2, 1908; President C. F. Burgess in the Chair.

THE PREPARATION OF CALCIUM ALLOYS FOR ALUMINOTHERMIC WORK.

By O. P. Watts and J. M. Breckenridge.

The use of thermit for the welding of pipes and rails, and for the repairing of broken machinery, has become so general throughout the world, that these applications of the aluminothermic process to engineering need no description. The uses of aluminothermy in chemistry and in metallurgy are, however, not so generally known, and a brief account of the process as applied in these sciences, and of some of the improvements made in it up to the present, may, perhaps, be necessary as an introduction to the experiments which form the subject of this paper.

When a mixture of an oxide with granulated aluminum in chemically equivalent proportions is strongly heated at one spot, a vigorous reaction often occurs, at the end of which the oxygen has combined with the aluminum, and the other metal has collected as a single mass in the bottom of the crucible. When neither the crucible nor the reacting materials contains carbon, the metal produced is, of necessity, carbon-free. Because of the almost universal tendency of aluminum to form alloys with other metals, it is necessary that this element be rather finely divided, and that the oxide to be reduced be slightly in excess of the amount required by theory for complete reaction. This reaction is usually started by placing in the top of the charge a small amount of a mixture of pulverized aluminum or magnesium with some peroxide. The mixture is conveniently kindled by thrusting a few inches of magnesium ribbon into it to serve as a fuse.

In this manner over 100 tons each of chromium and of manganese are produced annually, as well as considerable quantities of other metals and alloys.

It is necessary that the reaction shall furnish enough heat to melt both the metal and the alumina formed so that the scattered particles in which the metal is first formed may collect into a single mass. The temperature produced depends upon the difference between the heats of formation of the oxides to be reduced and of alumina, and to some degree upon the amount of charge used.

It is evident from these considerations that a successful reduction of those oxides having a heat of formation nearly as great as that of alumina cannot be obtained by the ordinary "Goldschmidt process." If the metal desired has an extremely high melting point, like tantalum, titanium, tungsten and some others, success is doubly difficult. For these reasons Dr. Goldschmidt had, up to 1902, failed to obtain in reguline form the elements barium, beryllium, boron, cerium, silicon, thorium, titanium, tungsten and uranium.

Several ingenious and more or less successful attempts have been made to overcome the difficulties just mentioned. In general these improvements have consisted in

(a) Supplying heat from an external source;
(b) Increasing the amount of heat liberated by the reaction;
(c) Rendering the slag more fusible.

Attempts have also been made to lessen the cost of the reducing agent by substituting cheaper materials for a part or all of the aluminum.

External heat has been applied in two ways: By preheating the whole charge to the ignition point, and by adding the heat of the electric arc to that of the reaction.

Although the oxides of boron, titanium and several other elements are not successfully reduced by aluminum, Dr. Goldschmidt, by substituting for a part of the above oxides, those of iron or manganese, has obtained alloys of these metals with boron, titanium and vanadium. Success is attained by the greatly increased heat of reaction and the lower melting point of the metallic product.

Holleman,[1] in order to obtain silicon, added sulphur and extra aluminum to the usual charge of that metal and silica, thus in-

[1] Rec. Trav. chim. Pays-Bas, 23, 380 (1904).

creasing the heat obtained from the reaction. K. A. Kuhne[2] added potassium chlorate, and later various peroxides[3] and persulphates, and to secure a highly fluid slag, added fluor spar and lime to the charge. E. Maemecke[4] substituted a compound of silicon or ferro-silicon and magnesium for aluminum, and also claimed the use of aluminum, calcium, barium, strontium and sodium mixed with the reducing agents above mentioned. It is evident that some, at least, of these claims had never been tried by the patentee. In 1905, H. Goldschmidt[5] patented a mixture of calcium and silicon as a reducing agent for the purpose of securing a very fusible slag, and later[6] mixed calcium with the aluminum used in thermit. Attempts have been made to use calcium carbide and silicon in place of aluminum in such reductions, but with very limited success. F. M. Perkin[7] has recently experimented quite extensively with calcium and calcium hydride as reducing agents, and claims to have obtained a regulus of fused tungsten by the reaction of calcium with wolframite. If the mineral were of average composition the ingot must have contained about 76 per cent. tungsten alloyed with iron and manganese, and in consequence have possessed a melting point much below that of pure tungsten. Even so, its production is a distinct achievement.

The aluminothermic process has also been applied very successfully by A. Colani,[8] by Matignon and Trannoy[9] and others to the preparation of silicides, borides and other chemical compounds which had previously been considered as belonging exclusively to the domain of the electric furnace. At first the only compounds obtained were those of moderately low melting point, and of metals whose oxides are fairly easy to reduce, but more recently silicides of tantalum, titanium, tungsten and zirconium have been produced by the aluminothermic process.[10] This means that experimental research upon the most refractory metals and

[2] British patent 20,884 of 1905.
[3] U. S. patent 878,210, Feb. 4, 1908.
[4] British patent 3,089 of 1906.
[5] French patent, 361,197.
[6] British patent 926 of 1906; U. S. patent 875,345, Dec. 31, 1907.
[7] Electrochem. & Met. Ind., Jan., 1907, p. 276; 1908, p. 31.
[8] Comptes rendus, **141**, 33-35 (1905).
[9] Comptes rendus, **141**, 190.
[10] O. Hönigschmid, Monatsch, f. Chem., **27**, 1069-81 (1906), and Comptes rendus, **143**, 224-6; Ed. Dufacqz, Comptes rendus, **144**, 848-50 (1907).

compounds can now be carried on by those who have not an electric furnace at their disposal.

The preparation of alloys of alumium, calcium, magnesium and silicon for aluminothermic work, was undertaken with the hope of obtaining reducing agents which would possess a somewhat higher heat of oxidation per unit of oxygen than aluminum, and whose mixed oxides would form a much more fusible slag than alumina. It was also thought that there would be a decided advantage, so far as fluidity of the slag is concerned, in having the particles of the different oxides produced in intimate contact. This will be the case, to a far greater degree when the metals are alloyed, than when the different oxides are formed from isolated particles of each metal, as in a mechanical mixture.

From previous experiments with aluminum-copper alloys, it was believed that several alloys could be produced from the above-mentioned elements, which would be brittle enough to be pulverized to any degree of fineness required. This is a decided advantage over aluminum, as the size of the reacting particles is an important factor in the velocity of reaction.

To what extent these anticipations were realized, and what unexpected difficulties were encountered, will be shown in the following brief account of the experiments.

Twenty-three different alloys of calcium with one, two or all three of the elements—aluminum, magnesium and silicon, have been prepared. Their composition is shown in the table opposite:

The alloys were made in an electric furnace of the granular-resistor type, by melting the constituents together in crucibles of Acheson graphite. The method of operation was as follows: The crucible was set in the furnace, sufficient calcium chloride added to form a layer over the metals when melted, and the elements put in in the following order: Aluminum, silicon, magnesium, calcium, each as soon as the one previously put in had melted. Since the temperature was always much below the melting point of silicon, this element was taken up only by solution. This was a rather slow process until the calcium or magnesium was added, when the silicon quickly dissolved. The alloy was stirred very thoroughly, and poured into a cast iron mould. There was little trouble from burning of the calcium

until this exceeded seventy per cent. In two attempts to prepare a calcium-aluminum alloy of over eighty-five per cent. calcium, the alloy took fire and was lost. The time required to melt and pour a charge of about a pound varies from five to twenty minutes, depending on whether the furnace was hot or cold when the charge was put in, and upon the amount of calcium added. Ten to twelve kilowatts was used for heating, although the cur-

No. of Alloy.	Formula.	Aluminum.	Calcium.	Magnesium.	Silicon.
1	. . . . .	75.	25.	. . . . .	. . . . .
3	. . . . .	74.5	25.5	. . . . .	. . . . .
4	. . . . .	45.	55.	. . . . .	. . . . .
5	. . . . .	. . . . .	30.	70.	. . . . .
6	. . . . .	60.	. . . . .	40.	. . . . .
7	$CaMg_2$	. . . . .	45.5	54.5	. . . . .
8	. . . . .	50.	30.	20.	. . . . .
9	AlCaSi	28.4	42.	. . . . .	29.5
11	AlCaMg	29.7	43.9	26.3	. . . . .
12	$AlCaMg_2$	23.5	34.8	41.7	. . . . .
14	$Al_4CaMgSi_3$	41.4	15.8	9.4	33.8
15	$AlCa_2Mg_2$	17.4	51.6	31.	. . . . .
16	. . . . .	93.8	6.4	. . . . .	. . . . .
17	. . . . .	90.	10.	. . . .	. . . . .
18	. . . . .	84.	10.	6.	. . . . .
19	. . . . .	67.1	12.9	. . . . .	. . . . .
20	. . . . .	80.	20.	. . . . .	. . . . .
21	. . .	80.	12.5	7.5	. . . . .
22	. . . . .	27.2	72.8	. . . . .	. . . . .
25	. . . . .	60.	. . . . .	40.	. . . . .
31	. . . . .	65.	. . . . .	. . . . .	35.
32	. . . . .	45.	. . . . .	20.	35.
33	. . . . .	60.	40.	. . . . .	. . . . .
34	40% Al+60 $CaSi_2$	40.	25.	. . . . .	35.
35	$Al_2Ca_3Mg_2$	24.3	54.1	21.6	. . . . .

rent was often interrupted for a considerable portion of the time in order to keep the temperature to the lowest limit that would melt the metals. The alloys containing only calcium and magnesium were troublesome to prepare, as they were less dense than the protective layer of calcium chloride.

In appearance these alloys vary greatly, from the homogeneous glass-like structure of No. 6 (60% Al, 4% Mg), to the coarsely crystalline structure of No. 9 (28.4% Al, 42% Ca, 29.5% Si), which appears to be a mass of flat crystals ⅛"x½". Their luster is metallic, and in most cases brilliant. They all decompose water

at rates depending mainly on the amount of calcium or magnesium present. The addition of three drops of concentrated hydrochloric acid to 15 c.c. of water containing the alloys causes a considerable increase in the rate of evolution of hydrogen, and with the silicon alloys, yields a spontaneously inflammable gas, probably partly SiH_4. This causes sharp explosions in the test tubes.

The stability of the alloys in air is remarkable. After two weeks exposure in the laboratory, only one has disintegrated to an appreciable extent. As this alloy, No. 22, contained 73 per cent. of calcium, its disintegration was to be expected. The other alloys appeared as bright as when made. This is in striking contrast to the rapid disintegration of copper-calcium alloys.

All of the above alloys, which contained 25 per cent. or more of calcium or magnesium were readily pulverized in ordinary crushing and grinding machinery. Nos. 11 and 15 took fire in the grinder at first, but with a little care, gave no further trouble. A series of calcium-aluminum alloys was made to determine the least amount of calcium which would render the alloy brittle enough to pulverize readily. At 20 per cent. calcium the alloy was not sufficiently brittle for this purpose. The upper limit of the brittle alloys was not reached, as the highest in calcium of all the alloys prepared was the most easily broken. This was not tried in grinding machinery as the quantity made was small.

The percentage composition given is that calculated from the amounts of the constituents originally weighed out, and is subject to errors of 2 to 3 per cent., as the balance used was for rough weighing only, and there was a variable amount of calcium chloride adhering to the sticks of calcium. Determinations of calcium in two alloys containing a high percentage of this metal showed the errors to be within the limits mentioned.

Experiments in the use of these alloys are now in progress, but are not sufficiently advanced to draw final conclusions in regard to them.

Attempts have been made to reduce the compounds MoO_3, MoS_2, WO_3, SiO_2, Fe_3O_4, Mn_3O_4, TiO_2 and mixtures of SiO_2 with MnO_2, of TiO_2 with MnO_2 and of TiO_2 with Fe_3O_4. The alloys so far tried are Nos. 8, 11, 14 and 15.

The first experiment was an attempt to reduce MoO_3 by alloy No. 8. The oxide was the usual fine powder of commerce and the alloy a mixture of all sizes that would pass a 20-mesh sieve. The reaction was very rapid, and was accompanied by the projection of melted material, flame and much smoke. At the end of the reaction the crucible was nearly empty, and contained no metal. Thinking that the sudden expansion of air contained between the particles of the charge might be responsible for much of the loss of material, the experiment was repeated in a vacuum cylinder constructed from a piece of 8-inch steam pipe. Less material was projected than before, but the loss was still great. Forty grams of well-fused molybdenum was obtained.

Several other experiments were tried in vacuo. SiO_2 was only partially reduced, yielding a brown product resembling silicon monoxide in appearance. A mixture of MnO_2 and SiO_2, reduced by alloy No. 11 (A_1CaMg), gave an excellent ingot of silicon-manganese, well separated from the slag. The yield was only 22 per cent. of the theoretical, probably due to the large amount of material projected from the crucible. In order to reduce the velocity of reaction, pulverized fluor spar and lime were added to several charges, with a slight improvement in the yield of metal. After eight trials in the vacuum cylinder, experiments under atmospheric pressure were resumed.

Reduction of a mixture of MnO_2 and TiO_2 by No. 15 ($A_1Ca_2Mg_2$), in pieces ¼ to ⅛ of an inch in length, was violent, with much flame and smoke, and the projection of some slag. Only a few globules of metal were obtained. Other reactions were tried with quite similar results. The only alloy that gave quiet reactions was No. 14 ($Al_4CaMgSi_3$). This acted much like aluminum itself.

As a last resort the charges were fired inside a closed steel cylinder, designed to withstand a pressure of 10,000 pounds per square inch. With this apparatus, several difficult reductions were carried out. Mixtures of the alloys with molybdenite in theoretical proportions failed to react, but on adding a large excess of alloy and enough calcium peroxide to oxidize it, an ingot of well fused metal was secured.[11]

[11] This addition of a mixture containing an alkaline-earth peroxide with the reducing agent to assist in difficult reductions, devised by one of the authors in 1905 (Bull. of Univ. of Wisconsin, No. 145, p. 313), has recently been patented by Kühne, as already cited.

The most difficult reduction carried out was that of rutile. By the use of calcium peroxide, a single button weighing 15 grams, and many groubles were obtained. The metal is hard, though not sufficiently so to scratch glass. It is not in the least malleable, and is broken by severe pounding with a hammer. In appearance it resembles freshly broken Goldschmidt manganese. A qualitative test shows the presence of aluminum, apparently in rather small amount. It is hoped that further experiments may lead to the elimination of this impurity. Until this is attained the reduction cannot be considered a success.

All attempts to obtain tungsten from WO_3 failed.

The cause of the violent nature of the reductions by aluminum-calcium-magnesium alloys, whether carried out in air or in vacuo, whether the materials were coarsely or finely pulverized, was, for some time, very puzzling. The following explanation is offered:

When all the products of reaction are non-volatile, and no gases are present, it would seem that mere rapidity of reaction should not throw half the material from the crucible. If the cause does not lie in the volatile nature of some product, nor in the speed of the reaction, it must be sought in the original charge, and it is here that the authors believe that the difficulty lies—in the low boiling points of calcium and magnesium. The boiling point of the latter is given at 1100°C,[12] and that of the former as about 1300°.[13]

Besides confining the charge in a gas-tight cylinder, another method of preventing this vaporization of calcium was tried. Since calcium silicide is a product of the electric furnace, it ought to be stable at a very high temperature. It should follow that if all the calcium put into a thermit charge is in the form of calcium silicide, none of the metal can be vaporized until the silicide is decomposed by oxidation. When a molecule is broken up by attraction from outside, that element in it which has the greater affinity for the destroying agent is not the one which will "get left" in the struggle for oxygen. It was therefore expected that the calcium would all be burned to lime without vaporizing.

Alloy No. 34 (40% Al, 60% $CaSi_2$), was prepared to test this

[12] Landolt & Börnstein's Physikalisch-chemische Tabellen.

[13] The Alloying of Iron and Calcium, A. Hirsch and J. Aston, this volume.

theory. In two reactions with Fe_3O_4, in open crucibles, there was no projection of material, and the reduction was very successful. The presence of this amount of silicon in the reducing agent, either free or combined, would greatly reduce the temperature attained. It is possible that the effect observed was entirely due to a diminished heat of reaction rather than to the reason assigned; yet the fact that the temperature was high enough for iron to be perfectly fluid, leads us to consider these experiments as evidence in confirmation of our theory. Further experiments are in progress upon the prevention of this supposed vaporization of calcium and magnesium from such alloys.

Several alloys have been used in the ignition mixture instead of aluminum or magnesium, and have proved more reliable for that purpose than either of those metals. This is probably due to their possessing a lower kindling point.

The cost per pound of materials entering into the alloys was: Aluminum, $0.43; calcium, $1.50; magnesium, $1.25; silicon, $0.15. The cost of materials in three of the alloys was: $1.14 per pound for No. 11, $1.36 for No. 15 and $0.58 for No. 14. Silicon appears to be the only cheapening material at present available for addition to aluminum or its alloys, when they are to be used for aluminothermic processes.

SUMMARY.

The results so far obtained in these experiments may be summed up as follows:

Alloys of calcium with aluminum and magnesium can be easily prepared up to a calcium content of 70 per cent.

Alloys containing 25 per cent. or more of calcium or magnesium can be readily pulverized.

In the absence of any considerable amount of silicon, alloys containing much calcium or magnesium react very violently in the reduction of oxides, and the yield of metal is small.

So far as tested, the addition of silicon to alloys of aluminum and calcium in the proportions necessary for the formation of $CaSi_2$, renders the reactions quiet, and greatly increases the yield of metal.

Experiments along the lines indicated are being continued.

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DISCUSSION.

Prof. J. W. Richards: It is a great satisfaction to me to see the aluminothermic process a commercial success. It may be well to recall that the first to reduce metallic oxides by an aluminothermic operation were the Tissier Brothers, who in 1858 made experiments in reducing metallic oxides by aluminium. They made the very natural mistake, however, of heating the whole mass to the ignition temperature in a furnace, and when they did so the reaction was so violent it blew the crucibles and furnace all to pieces. Goldschmidt modified that reaction so that it proceeded quietly and quite a safe operation resulted.

I wish to add what I can to the proposition to call this class of processes by another name. We have alumino-thermic, we have silico-thermic and we have calcio-thermic. I think the whole operation should be called metallo-thermic, or generally a metallothermic reaction. It is a solecism to apply the word "aluminothermic" to reactions of calcium and silicon. The idea is to apply the reaction to thermic processes, using a metal as the reducing and heat supplying reagent, and I think it would be an improvement in our nomenclature to call them generally metallo-thermic operations, and hope it will be done before it is too late.

Mr. Henry D. Hibbard: I might say a word in addition to this. Messrs. Greene and Wahl (Mr. Wahl is secretary of the Franklin Institute of Philadelphia) did some reduction of metals by aluminum, I think in the early 90's. I used to have a pocket piece of metallic manganese that was made that way. Manganese and silicon is what they were chiefly after. This piece of manganese was different from what I get now. It was a bright metallic metal, about the color of silver, I would say, but it broke with a conchoidal fracture, and not a granular fracture; it was so hard it would scratch glass. I do not think that it was ever made on a commercial basis, but it was very interesting at the time to some of us who were interested in metallic manganese, especially manganese which contained no carbon. I believed that they were the first to make manganese practically free from carbon. Two of the processes were patented at that time, and the patents have about expired, I think. I was surprised, from what Professor Richards said, to hear it had been done a good many years before that.

MR. WATTS: I found the process was not commercially successful, and, judging from the description of the manganese, I should think, judging from the description of their product, that it was probably an alloy of manganese containing aluminum, which Messrs. Greene and Wahl produced. I should judge that from its great brittleness and the whiter color than the manganese which we have to-day.

Replying to Mr. Betts' question, in regard to the possible use of these alloys mechanically, I do not see any particular use for them. They are too brittle. The object of this work was to get alloys that were brittle, and these are not what one would expect to find useful for mechanical purposes, although no doubt alloys can be made by changing the proportions very much which will be applicable to mechanical use.

PROF. J. W. RICHARDS: Dr. Wahl used a considerable amount of cryolite as a flux, and that contains a great deal of silica. Undoubtedly there was silicon introduced into the alloy that way, which would give it a conchoidal brittle fracture. I ask Dr. Watts whether the use of this as a flashlight powder would possibly not be practicable.

MR. WATTS: I think that would be very practicable. I think it would react violently, and give an intense heat and light, and I think it would be quite possible to use it for that purpose.

PROF. A. W. SMITH: If there are two names for this process, inasmuch as the substances are not metals, why not call it elemento-thermic, and that would cover the whole thing.

MR. RICHARDS: The word elemento-thermic is rather too clumsy for ordinary use, and, in fact, covers far too much to be properly used in this connection. I think "metallo-thermic" really covers the needs of the case, and would be a satisfactory improvement on the too limited term "alumino-thermic."

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., April 30, 1908; President C. F. Burgess in the Chair.

INDUSTRIAL APPLICATIONS OF ALUMINUM.

By E. Blough.

It is with some hesitation that I present a paper of this character before this society. All the other papers represent a great deal of research, while this one deals purely with the commercial aspect of aluminum. This metal is one of the oldest of the electrochemical products—the present process dating from 1886.

I thought it might interest the society to be told how aluminum has grown from a laboratory experiment to one of the practical metals of the world.

In its early history this metal was hampered by the extravagant claims made for it by the general press. It was said to be lighter than wood, that it did not corrode, that it was stronger than steel and was practically insoluble in most solvents, all of which is not true. On account of these statements attempts were made to use the metal where it was wholly unsuited. Partly by elimination, but largely by the exercise of more judiciousness, its application to the useful arts has now settled down to a more sane basis.

Aluminum is used either alloyed or pure and this statement gives the uses a sort of natural classification. The alloys are used largely for castings, or it is perhaps better to say that practically all castings are made from alloys. It is impossible to enumerate all the wide uses of aluminum castings. Among the more important are automobile parts, such as engine bed, crank case, transmission case, rear axle-housing, running board, fan, seats, bodies, etc.; electrical instruments, such as meter frames, meter covers and pipe fittings, cooking utensils, etc.

Another important use for either pure aluminum or aluminum alloy with either iron or silicon, or both, is as a deoxidizer for steel, although only a few ounces are used per ton of steel, yet the aggregate amounts to many thousands of pounds of the metal

per year. One novel use in this connection is in securing sound steel castings. Small pieces of aluminum are placed in thin parts of the mould or parts far from the gate; when the cooled metal comes in contact with the aluminum a reaction immediately results, with the consequent reheating of steel. The metal flows on, filling the mould and producing a sound and perfect casting.

Another class in which aluminum is used is in wrought forms. Both pure and alloyed metal are used for working, although the alloyed metal for this purpose usually contains less of the alloying ingredient than do the casting alloys. Among the forms which find the most varied use is sheet metal.

Among the uses of sheet aluminum are sheet automobile bodies, signs, novelties, cooking utensils, steam-jacketed kettles, pans in stearic acid and glycerine manufacture, candle factories, soap factories, candy pans and kettles, wine and yeast vats, car linings, cameras and other similar uses.

Aluminum tubing is coming into wide use. Some of these applications are in acetic acid manufacture, photographic chemical supplies, nitric acid condensers, sulphite pulp mills, ammonia concentrators, vulcanizing mandrels for rubber and bimetallic tubing for surface steam condensers.

Besides the wrought forms are the rod and shapes. Rod is produced by the usual process of rod making, while the shapes are generally extruded. Rod is used in the manufacture of small parts, automatic machine work, etc., either for its lightness, electrical conductivity, non-magnetic properties or other mechanical qualities. Aluminum shapes find great popularity on account of their adaptability to various uses. One important use is for moulding on automobile bodies, others are trolley bow shoes, angles, gaskets, etc.

Aluminum is widely used as high tension feeders and transmission lines. A large part of the power from Niagara Falls is distributed through aluminium cables. Street and interurban railway lines throughout the United States use aluminum as feeder lines. Electric lighting companies are using this metal to distribute light and power, while many of the high tension lines of the far West are of aluminum cable.

Aluminum bus-bars are in use to some extent—notably at Niagara Falls, for carrying current up the face of the cliff.

Beside cheapness, large cooling surface and ease of handling are the important advantages.

In drawing and spinning, aluminum finds special favor. It can be drawn into forms with few operations and little annealing, yet when of proper temper or suitably alloyed a very stiff finished product results.

From this rather brief outline you can see the rapid strides aluminum has made. To replace the oldest metals known is not an easy task, yet in less than twenty years on the market as a commercial metal, aluminum has made a place for itself among the useful metals.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 2, 1908; President C. F. Burgess in the Chair.

THE NATURE OF THE SURFACE FILM FORMED ON ALUMINUM, AND THE ALUMINUM-MAGNESIUM CELL.

By H. T. Barnes and G. W. Shearer.

The electromotive force developed between aluminum and magnesium has been described in two papers[1] before this society, when it was shown that this depends on the action of oxygen dissolved in the electrolyte on the surface of aluminum.

Recently we have shown[2] that aluminum reacts with dissolved oxygen to form hydrogen peroxide, and hence the addition of this reagent to the cell, which was shown to augment the e. m. f., only increases the concentration of the substance already formed. The development of peroxide can take place, as Bancroft suggests, according to the following reaction:

$$2Al + 6H_2O + 6O = Al_2(OH)_6 + 3H_2O_2.$$

This is important in suggesting to us the nature of the film which is formed on the surface of aluminum when exposed to moisture and which plays so important a part in the action of aluminum in the alternating current rectifier.

If a current is passed through the cell, making the aluminum an anode, then the reaction is hastened, more peroxide is formed and more hydroxide produced. If the aluminum is cathode, as it is in the normal working of the cell, then the peroxide is reduced and the film removed. Hence, when short-circuited, the resistance of the cell is much reduced and the current increased, the e. m. f. being that produced by the presence of free hydrogen peroxide around the aluminum.

Schulze[3] has recently made a study of the anodic behavior

[1] Trans. Am. Electrochem. Soc., **3**, 95 (1903); Ibid, **12**, 54 (1907).
[2] Jour. Phy. Chem., **12**, 155 (1908).
[3] Arn. der Physik., **24**, 43 (1907); Ibid, **25**, 775 (1908).

of various metals similar to aluminum, and has shown the phenomenon of asymmetric conductivity in a number of other metals. This he attributes to a thin layer of gas or oxide on the surface, which gives rise to various effects depending on whether the oxide is conducting or not, or whether it is soluble. Antimony and bismuth exhibit asymmetric conductivity to a very marked degree, as does magnesium, and a number of the rare metals.

The fact that hydrogen peroxide may be produced in measurable quantities when aluminum is immersed in pure water charged with oxygen, and not in oxygen free water, indicates directly the nature of the surface film that is formed and which has been the subject of so much discussion by previous observers.

McGill University,
April 30, 1908.

DISCUSSION.

Dr. W. R. Whitney: Mr. President, can you give us any information on the action of the aluminum rectifier?

President Burgess: The aluminum rectifier was at one time very promising, but the advent of the mercury rectifier has overshadowed it. Rectifiers of the aluminium type have irregularities, the electrodes do disintegrate and there are certain electrolytic changes in the electrolyte. Electrolyte rectifiers have been known to give continuous satisfaction to the users for long periods in the connection with X-Ray work and the like, but I do not know that they have been introduced into general commercial practice.

Dr. Whitney: I did not have data of any rectifier of that kind. I find a great many aluminium rectifiers which have been used over a short period of time, but looking for actual data on the rectifier to determine the life of the common rectifier, I find it very difficult to discover any such data, and I thought that this society ought to be interested in it.

I hoped possibly that some of the gentlemen who work on rectifiers might have studied the matter to the extent of determining whether the quality of the aluminum was one of the de-

termining factors in the life of the rectifier. The two which I have seen died on my hands, and they died because the aluminum corroded away, as Mr. Burgess pointed out. It seemed natural to suppose that was due to inequality in the aluminum. Theoretically, aluminum rectifiers are beautiful, but practically they are not. I would like to know if any of the members present have done any work with aluminum rectifiers.

PRESIDENT BURGESS: I will say my apparent hesitation in speaking of my experience is not due to any commercial reasons, but it is because I consider my work on that a failure as far as producing successful results is concerned. I do not like to speak of failures, although I think one of the most important line of papers we could have would be a description of our failures, something we do not get. The papers which we have cover some of the things which we have done, and many of the things which we are going to do, but describe very few of the attempts in which we have failed, and I think that papers of that sort would be of very great value.

There are members of our Society who can give information with reference to the effect of various impurities in aluminum on its durability for rectifying purposes. Impurity does have a good deal to do with it, and some materials added to aluminum seem to be somewhat beneficial. Mr. Hambuechen and Mr. C. I. Zimmerman and Mr. Mott have data of this sort, and would undoubtedly be willing to impart it to anyone interested.

MR. CARL HERING: I am glad the President said what he did about the publication of failures. I heartily agree with him that if we would describe our failures more than we are in the habit of doing, it would be of great benefit to others. I have no doubt that it has often happened that, because people do not publish their failures, others have repeated the same experiments and also failed, which experience would be avoided if failures were published.

As an illustration of the advantage of making public our failures, I call attention to a case which occurred in the early history of this society. One of our members described some failures he had encountered in a certain line of experiments. The subject was then discussed by the society, and suggestions were made with the result that the difficulty was overcome, which was of

great commercial advantage to the member who had described his failure.

Dr. H. T. Barnes *(communicated):* We can hardly expect the aluminum in the rectifier to withstand the continued action of the current. Decomposition of the surface film does not appear to be complete, and in consequence an excess of hydroxide is produced, which accumulates in the electrolyte with slow disintegration of the metal. The protection supplied by the film to the metal is much greater at low temperatures than high, and ceases altogether in a hot solution, because the adhesive properties of the film become much less as the temperature rises.

The aluminum we have used in our experiments was supplied as pure by the Canadian Aluminum Works. We have not paid particular attention to the effect of impurities, but we believe that the disintegration of the metal would be merely hastened by local action.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 2, 1908; President C. F. Burgess in the Chair.

THE USE OF DRY CELLS ON IGNITION SERVICE.

By J. W. Brown.

With the rise of the great gas and gasoline engine industry, the problem of providing a suitable means of exploding or igniting explosive gaseous mixtures has become a very important one. In all modern gas or gasoline engines, the ignition is accomplished by means of an electric spark either drawn between two separating contact points or surfaces or forced to jump between two stationary points within the cylinders of the engine at definite positions in the engine cycle. The electrical energy required to produce these sparks is practically always obtained from an electrical generator, such as a dynamo or a magneto generator or from a battery. In this paper, the discussion will be confined to ignition service in which the electrical energy is obtained from a battery, and especially from a dry battery.

The dry battery was early in the ignition field, and is at the present time an important competitor in that field, notwithstanding the fact that it has been, and still is, used in a very inefficient manner. The wasteful character of ignition apparatus used with dry batteries, the imperfections of earlier dry cells, and the presence on the market of many brands of dry cells of uncertain value have, however, served to turn some operators of gas or gasoline engines to the storage battery. Of necessity, this will be the case to a far less extent as soon as the faults of battery ignition apparatus have been corrected and engine operators have reached the practice of selecting dry cells of standard brand and of using them connected up into a battery of a size and form suitable to the service.

Before considering the use of dry cells on ignition service, it is of importance to note a few things concerning the usual

type of ignition apparatus, namely, that consisting of a spark plug, a transformer spark coil, and a make-and-break device or timer. Such an apparatus is shown in the following figure.

Here it is the function of the timer to close the dry battery circuit successively through the primary coil of each of the four spark coils at the proper moments in the engine cycle, maintaining each contact for a sufficient period of time to allow the current to rise to such a value as to be capable of being transformed into one which will pass the gap in the spark plug in the form of a spark, and thus ignite the explosive mixture of gases in the cylinder of the engine. Evidently if the battery

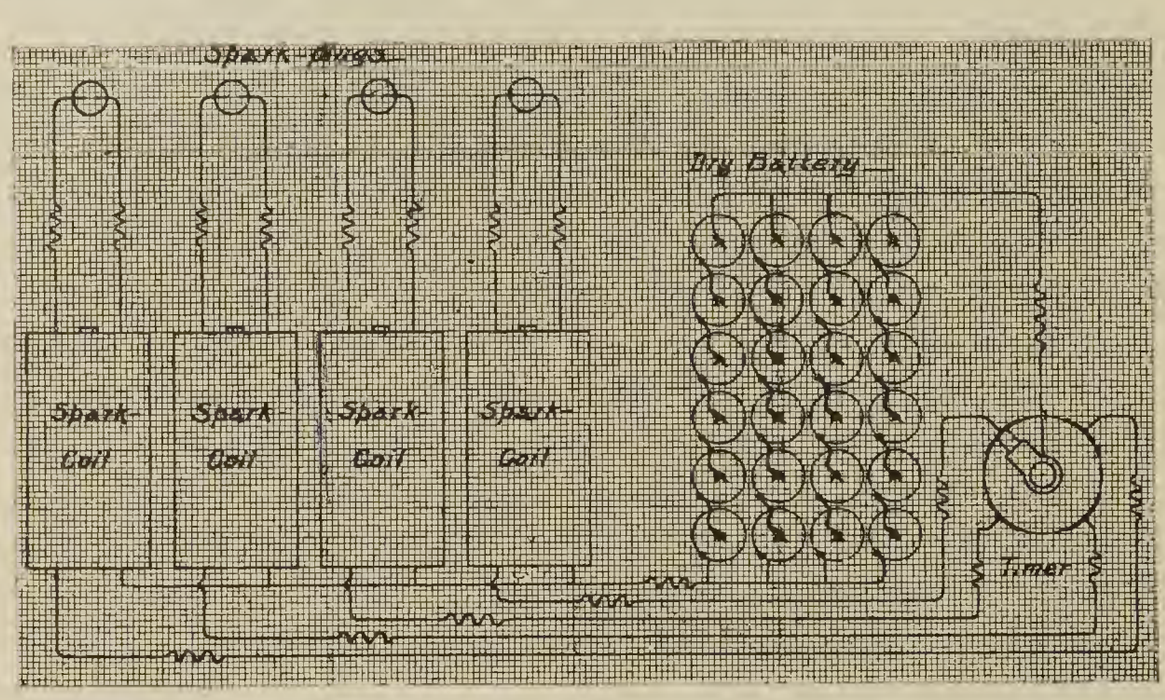

Fig. 1.

circuit is closed through the coil for a longer period than this, or if the spark coil is adjusted or designed to draw a greater current than the one mentioned, a waste of battery energy will result. The battery, timer and spark coil should, therefore, be adapted to each other in the efficient and economical production of the spark necessary to cause certain ignition. Unfortunately, this is not the present practice. As a result, we have batteries, timers and spark coils connected up together and put into service with little thought as to how they will work with each other.

From the standpoint of the efficient use of dry battery energy, the usual type of timers are faulty in having excessively long periods of contact variable with the speed at which the engine

is running, and the usual types of spark coils are faulty in drawing too much energy from the battery per spark and in producing too many sparks per explosion, especially at low speeds. The magnitude of this waste is considerable, as will be evident from the following statements:

Satisfactory ignition can be produced with a contact in the timer of a duration of about 0.005 second and with a single vigorous spark per explosion at all speeds of the engine. The resulting drain on the battery corresponds to a continuous current of from 0.01 to 0.05 ampere, according to the speed of the engine, the drain decreasing in direct proportion to the decrease in the speed of the engine. In spite of these facts, which are well proven by actual service, the usual or most-used types of timers produce contacts varying from about 0.01 to about 0.05 second in duration, and the most-used types of spark coils produce sparks varying in number from about 4 to about 15 per explosion, according to the speed at which the engine is running. The resulting drain on the battery is nearly independent of the speed at which the engine is running, and usually corresponds to a continuous current of about 0.5 ampere when the vibrator of the spark coil is properly adjusted. Moreover, it often happens that the drain is increased to several times this value by a faulty adjustment of the vibrator alone. In one particularly bad case, it was found to correspond to a continuous current of over two amperes. These statements may be illustrated with the aid of the apparatus shown in Fig. 2.

It consists of two axles with pointers so attached that when they are made to revolve, the pointers sweep over dials A and B in a manner similar to the hands of a clock. As the pointers sweep over the dials, their outer ends pass within, and about ⅛ inch from, brass rings secured to the dials. The apparatus is also provided with two milliammeters, A and B. The axles are motor-driven, and the speed is regulated by means of a strap-brake. The sets of ignition apparatus to be studied are placed as shown in the figure, and are so connected up that the dry battery circuit can be closed through ammeter A and ignition apparatus A, or through ammeter B and ignition apparatus B, or through both simultaneously. The secondary terminals of apparatus A are connected to the pointer and ring respectively

on dial A, and those of apparatus B are similarly connected to the pointer and ring on dial B. When now the battery circuit is closed through the two sets of ignition apparatus, and the

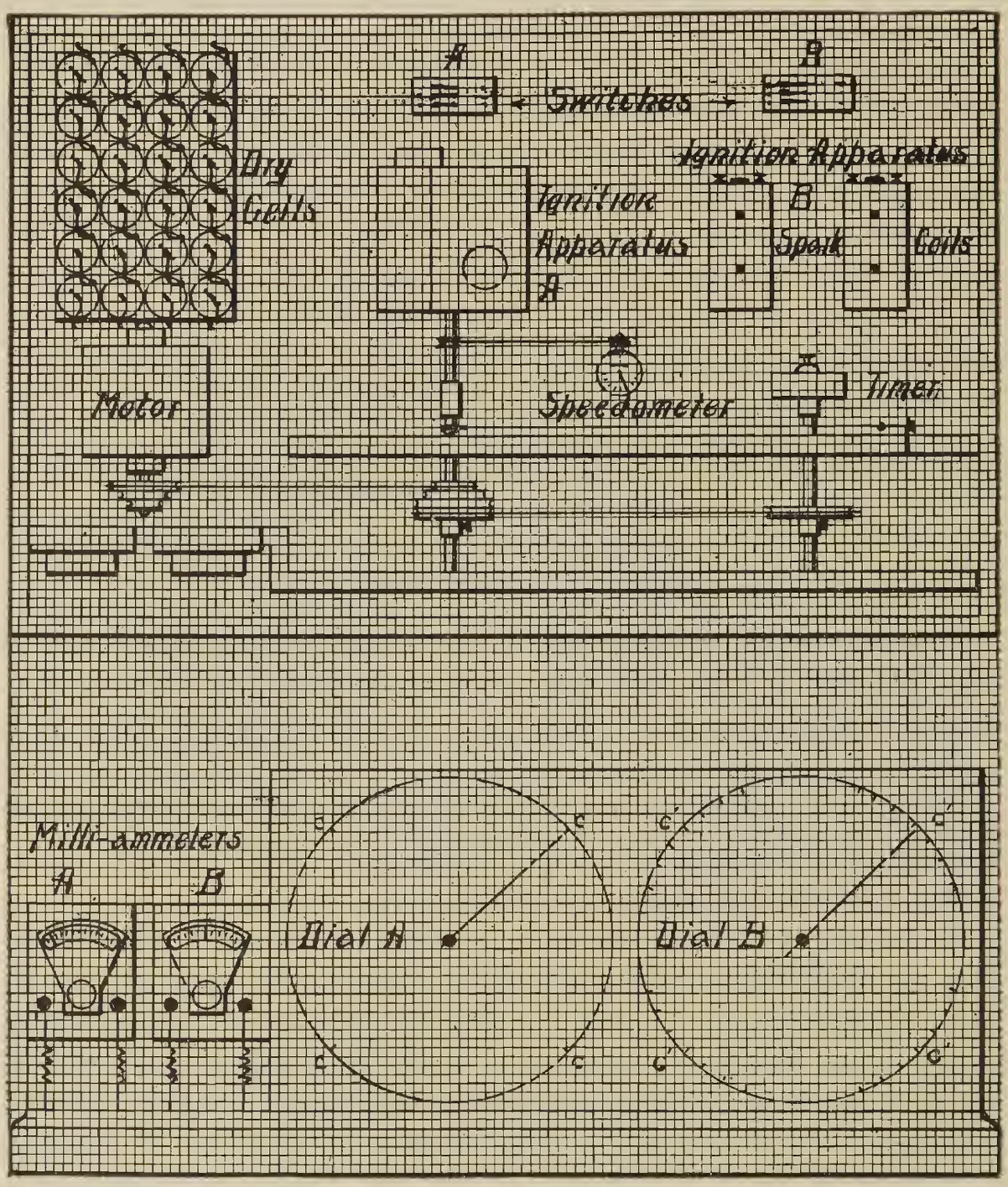

Fig. 2.

axles are made to revolve, sparks pass between the pointer and ring on each dial when contact is made through the timer, and the ammeters indicate the drain on the battery made by each set of apparatus. The number of sparks per explosion, and the

drain on the battery can therefore be easily determined at any engine speed and for any adjustment of the vibrator of the spark

In the figure, ignition apparatus A is provided with a mechanical make-and-break device, making a contact of very short duration, independent of the speed, and producing a single spark for each of the four contacts (for a four-cylinder engine) represented. Milliammeter A has been drawn to show the low drain on the battery. Ignition apparatus B is a far more common type, consisting of spark coil with an electro-magnetic vibrator and a timer which produces a contact of long duration variable with the speed at which the axle is revolving. The number of sparks obtained per explosion in each of the four cylinders of the engine at 400 revolutions per minute is indicated by the short dashes on the dial, and the drain on the battery is indicated by milliammeter B. The first spark in each series is the one which produces the explosion, the remaining sparks representing waste of battery energy. The number of useless sparks varies inversely with the speed at which the engine is running.

It should be mentioned in this connection that the Weston milliammeters are entirely incapable of indicating directly the real or intermittent character of the current drawn from the battery by the ignition apparatus, although they are capable of indicating closely the continuous current to which the impulse current is equivalent. This has been shown to be true by means of a coulometer placed in the circuit. The real significance of milliammeter readings taken in connection with ignition service deserves special emphasis, for the reason that such readings are generally considered by gas engine operators to indicate the real current drawn from the battery, and have led to much confusion.

This brief and incomplete discussion will suffice to show that, even when properly used, the usual types of such apparatus waste several times as much battery energy as they utilize in producing the ignition, and that those who use battery ignition should pay particular attention to the choice of ignition apparatus.

Turning to the dry battery itself, attention should be called to several important points concerning its ability to furnish electrical energy for ignition work and concerning the number and arrangement of cells in it which is necessary for economical

and reliable service. Great confusion exists among users of dry batteries as to the actual requirements of ignition work. As a consequence, dry batteries are generally tested for their fitness for such service in a wholly unreliable manner. Briefly stated, such work requires not only that the battery shall be able to furnish a given quantity of electrical energy, but also that it shall be able to furnish it in the form of a rapid succession of high amperage impulses, corresponding approximately to a two-ampere impulse through a resistance of about 0.5 of an ohm. Initial amperage and initial voltage readings, while indicating something in regard to the condition of a dry battery, fail utterly to disclose the ability of the battery to give a long and satisfactory ignition service. Furthermore, a continuous service test through such a resistance as will permit the passage of a current equal to that indicated by the milliammeter during actual service, also fails to show the fitness of a dry battery for ignition work. The only method at present available requires the actual determination of the period during which the battery is capable of producing the rapid succession of impulses required by the service when used with a particular type of apparatus. It therefore follows that the effective internal resistance, not of the unused battery, but of the battery while on service is of an importance second only to the available energy in determining the value of the battery for gas engine work, and the size and arrangement of cells in the battery necessary for best results. This is illustrated by the discharge curves given in Fig. 3.

In this figure, the full lines represent the discharge curves of a fresh dry cell giving an initial amperage of 20 amperes, and the dotted lines represent similar curves of a dry cell after about six months in storage, giving an initial amperage of 10 amperes. In each case, the upper lines represent the decrease in working voltage when the cells were discharged through a resistance of 8 ohms, and the lower lines represent the decrease in impulse amperage obtainable through a resistance of .08 of an ohm during the test. Although this test does not correspond exactly to ignition service, it does approximate such service, and serves to show the lack of a fixed relationship between the working voltage and the impulse amperage during the discharge. It will be noticed that the two cells are practically equal in respect

to their ability to furnish electrical energy continuously and at a low rate, but are very different in respect to their ability to furnish this energy in the form of impulses of about 2 amperes each. Furthermore, the two cells are practically equal in respect to their ability to furnish the energy in the form of impulses ranging from 0.5 to 1.0 ampere each. In this connection, it should also be mentioned that a similar difference may be found between two perfectly fresh cells of different constructions, even though

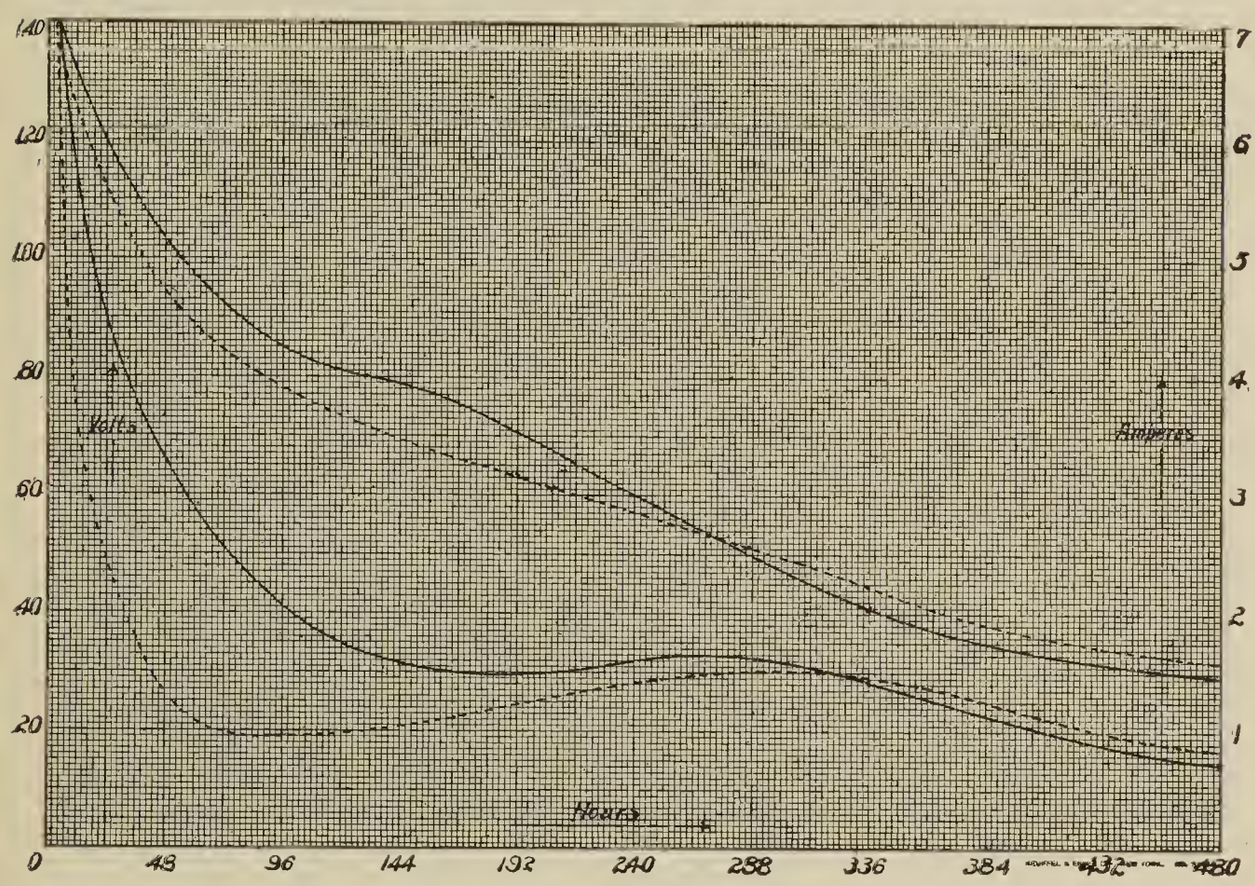

FIG. 3.

the initial amperages and voltages are substantially identical. Evidently this difference is due to the difference in the rate of increase of the total internal resistance or impedance during discharge, and is only developed by actual discharge. Corresponding to the results obtained on the above test, the one kind of cell is, and the other is not, capable of giving good ignition service when used according to present-day practice, in the form of a single battery of four to six 6-inch cells. Furthermore, both kinds of cells are capable of giving good ignition service for a much longer period per cell than usual when used in the

form of a battery composed of several sets of cells connected up in parallel. This may be demonstrated by means of a gas engine, or by means of the sparking apparatus shown in Fig. 1. That even in the case of perfectly fresh cells the length of service per cell is greatly increased by the use of such a battery, is evident from both Fig. 3 and Fig. 4.

In the latter figure, the dotted curves represent the drop in voltage of four batteries of dry cells, of four 6-inch cells each in series, when discharged one after the other through a 48-ohm

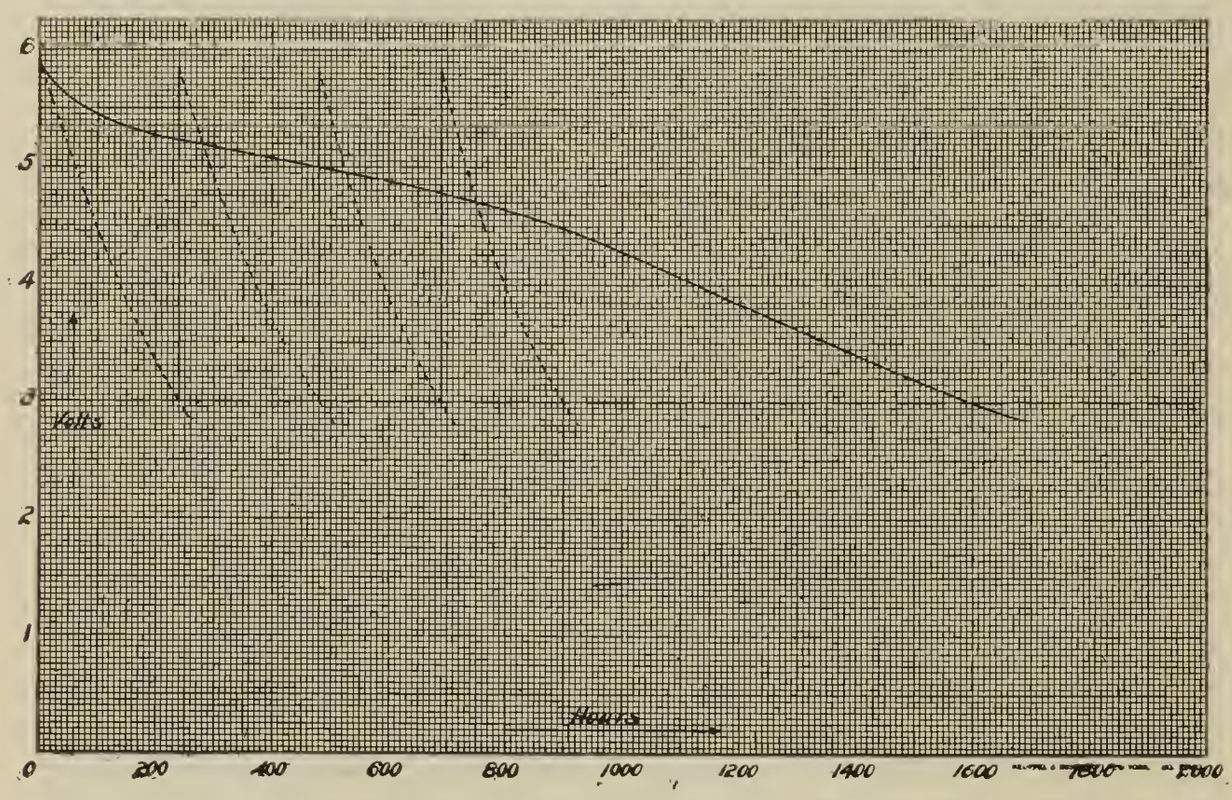

Fig. 4.

circuit. The full line curve represents the corresponding drop in voltage of a single battery composed of four sets, of four 6-inch cells each, connected up in parallel, when discharged through the same resistance. The drain per cell in the latter case was therefore but about one-fourth of the drain per cell in the single series batteries. As a result, the curves in the figure show a gain of nearly 100 per cent. in service life by using the sixteen cells in the form of a single series-parallel battery, instead of in the form of four smaller series batteries. It is a natural conclusion, from such results, that, both in respect to reliability and in respect to the length of service life per unit cost,

dry cells of the 6-inch size should not, except in the case of an emergency, be used in the form of a single series battery with present-day ignition apparatus. They should, on the contrary, be used in the form of series-parallel batteries, consisting of as many as four sets in parallel whenever possible.

Practically all dry battery troubles not caused by the use of ignition apparatus poorly designed or poorly adjusted may be located in the use of a battery of a form and size not adapted to the service required of it. Excluding these sources of trouble, which can be practically eliminated, dry cells made by manufacturers of high reputation are capable of furnishing electrical energy for gas and gasoline engine work with an economy and a reliability exceeded by no other means now in general use.

DISCUSSION.

President Burgess: Our published transactions contain a number of papers dealing with various forms of cells, both primary and secondary. We have a considerable number on the standard cell; but the previous speaker has opened up a new line of discussion which treats of perhaps the most important type of cell we have, the dry cell. The use of the dry cell in this country has reached enormous proportions. I have endeavored to estimate something of the number used in this country, and from very poor data I figured out somewhere between thirty million and fifty million per year.

The author whose paper has just been presented has pointed out a number of interesting things, and one of them is that there is no quick test which can be applied to a battery from which we can draw a definite conclusion as to what that battery or cell is going to do in its regular work. Is there discussion on this paper?

There are a lot of interesting electrochemical problems which I had hoped to speak of, but which I will not do now on account of lack of time. The dry cell is certainly an interesting subject for study from the standpoint of the electrochemist.

Mr. Carl Hering: Instruments of the movable coil, permanent magnet type, do not give correct indications for such very

intermittent currents as those in cases of this sort. For accurate measurements, instruments of the hot wire or electrodynamometer type would have to be used.

Dr. Brown: Weston milliameters, however, indicate closely the average current which is equivalent to the actual intermittent current flowing through the primary circuit of the spark-coil.

Mr. R. Fleming: At first sight I thought this paper was more suitable for presentation before the electrical engineers. The latter part of it, however, relates to electrochemical engineering. I wish to agree with Mr. Hering that the Weston instruments will not indicate properly the impulse current, and that nothing short of an oscillograph will do it.

Regarding the application of the dry battery for ignition purposes, I wish to suggest that the manufacturers of batteries are distinctly at fault. In the first place, they make no attempt to standardize the battery practically, and they depend on miscellaneous manufacturers to pick out any sort of coil to go with their batteries. I should say offhand that most of the cells were entirely too small to do the work, and manufacturers depend on the intelligence or lack of intelligence of the operators to make suitable combinations, which they will not do.

President Burgess: I agree with the last speaker (Mr. Fleming). The battery manufacturers are at fault in not standardizing battery practice better than they have. When making tests of batteries to be used for ignition service it is the practice of the users of these batteries to short circuit the cell through an ampere meter, and it is the common belief that the higher the amperage, the better the cell, and thus for commercial reasons, that belief being held, the battery manufacturers naturally try to make a high amperage cell, which will still give good service. It is possible to make a dry cell which, on short circuit, will show, in one of these ordinary No. 6 cells, from 20 to 30 amperes, whereas in actual use, as pointed out, the current that is drawn from them is much less than one ampere. This high test of amperage can only be secured through the sacrifice of durability and some of the other desirable properties of the cell.

Mr. Brown: I cannot agree with Mr. Fleming or Professor Burgess in their remarks concerning dry cell manufacturers.

These remarks may apply to some small manufacturers, but they cannot justly be applied to the large manufacturers of dry cells. After several years' study of the dry call industry, it is my opinion that the manufacturers of over three-quarters of the millions of dry cells annually produced in this country are not distinctly at fault in their methods of handling their problems. It is not true that they make no attempt to standardize their product, or that they do not concern themselves with the manner in which dry cells are used. On the contrary, there are but few industries in which more work is in progress along such lines than in the dry cell industry. Testing and research laboratories which easily rank among the finest industrial laboratories in the country are maintained to secure the highest development of the dry cell and to assure high standard quality and efficiency of all dry cells produced. For several years an extensive educational campaign in the proper use of dry cells has been carried on. I wish to say further that both of these lines of effort have been successful and are constantly bearing fruit, any off-hand statements to the contrary notwithstanding. Thousands of dry cell users are now looking beyond superficial initial amperage and demanding instead long service, and are using greater care in the selection of ignition apparatus and the brand and size of battery to use with it.

Prof. J. W. Richards: I think Mr. Brown has said that the coulometer checked up with the instrument.

Mr. Brown: I think I was misunderstood in that case. I did not mean that the needle swings forward and indicates the full value of each actual impulse, but that it swings to a position, representing pretty closely the amperage of a continuous current which is equivalent to the intermittant current flowing in the primary circuit of the spark-coil. In thus indicating the rate at which electricity is drawn from the battery by the spark-coil, it gives results agreeing closely with those obtained with the aid of a coulometer in the circuit. The individual impulses in the primary of the coil may vary anywhere from about two to about six amperes, according to the size of the battery and design of the coil.

Mr. Hering: I understand the readings given represent the average deflection.

Mr. Brown: About the average, but they do not represent the actual form in which the current is drawn from the battery. They represent the average of a series of periods of high impulse and periods of rest.

Mr. Hering: Have you any idea of the time interval of the current impulse, as compared with that of the period of rest?

Mr. Brown: The duration of an individual impulse is something in the vicinity of .005 of a second in the case of vibrator coils. It varies with the adjustment of the vibrator and the current flowing in the coil, but this value indicates the order of magnitude.

Mr. Hering: How many impulses are there per second?

Mr. Brown: In the case of the vibrator coil used on the apparatus shown, 40 to 50 sparks are obtained per revolution, when the axle is making about 400 revolutions per minute. The number of impulses per second can be obtained from these values.

Mr. Brown: I would like to add a few words in reference to high amperage of dry cells intended for ignition service, along the line touched upon by our President. It is true that the current which, according to the milliameter, is required for ignition service is generally only about .5 of an ampere. It does not, however, follow that dry cells giving low initial short circuit amperages of 1 to 6 amperes are capable of giving good ignition service. As a matter of fact, such dry cells, when used in the form of a single series battery, are not capable of properly operating the usual types of spark coils even if they are capable of giving a continuous current of .5 of an ampere for a long period. This is due to the fact that such cells cannot give the energetic impulses required. It is therefore essential that dry cells intended for ignition service be designed to give a succession of high amperage impulses for a long period during actual service. Incidentally, such cells will give an initial short circuit amperage of considerably over 10 amperes. I say incidentally because there is very little relation between this initial amperage when greater than 10 amperes and the short circuit amperage during service. Cells giving 30 or more amperes initially generally give a lower short-circuit amperage service than cells giving 10 to 20 amperes initially.

Mr. Hering: The heat of the spark would seem to depend on

the energy or watts in the spark itself. An ampere meter does not indicate the energy or watts taken from the battery; if, for instance, the battery is short circuited it gives a certain current, but it has practically no voltage, and hence there is little energy. To get an idea of the energy which is given by the battery or set free in the spark, it is necessary to measure the voltage also. Moreover, the current and voltage measurements must be made absolutely simultaneously or else the results may be far from correct.

Mr. Brown: It is, of course, true that the quantity of electrical energy transformed into heat at the spark plug determines the "hotness" of the spark, and it is also true that the quantity of electrical energy drawn from the battery cannot be expressed in terms of amperes. It does not follow, however, that current and voltage must be measured absolutely simultaneously in order to obtain results of sufficient accuracy for all practical purposes. By relying on Ohm's law, the measuring of the current alone is sufficient since, with a given coil at a given adjustment, the resistance may be considered constant. If the value of the resistance is desired it can be measured easily once for all.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., April 30, 1908; President C. F. Burgess in the Chair.

THE TEMPERATURE FORMULA FOR THE WESTON STANDARD CELL.

By F. A. Wolff.

INTRODUCTION.

The more recent work on the standard cell has demonstrated that the Clark and Weston types are both reproducible to a very high degree of accuracy, and that, when properly set up, both may be depended on within a few parts in 100,000 for a year at least. As these qualities, in connection with the concreteness and ease of reproduction of the standard cell, seem to point to it as the logical choice for the second fundamental electrical unit, a redetermination of the temperature formulæ has been undertaken. On account of the very small effect of temperature variations on its electromotive force, and the absence of cracking at the amalgam terminal, distinct advantages over the Clark cell, an investigation of the Weston cell was first made. A redetermination of the temperature formula of the Clark cell will, however, also be undertaken.

HISTORICAL REVIEW.

The first statement regarding the temperature coefficient of the Weston cell is found in the specifications of the patent issued to Dr. Edward Weston, who justly claimed as a special advantage of the cell, its small variation in electromotive force with temperature changes which he stated to be less than .01 per cent. per degree.

The results of Dearlove[1], obtained with several lots of cells in which apparently no excess of cadmium sulphate or mercurous sulphate was employed, were quite irregular. Three cells

[1] Electrician, 31, 645 (1893).

of the first lot, in which the amalgam "was estimated to contain one part of cadmium to five parts of mercury," had an e. m. f. greater than 1.03 volts, and differed from each other by as much as 2 millivolts. In addition the e. m. f. of the cells was variable, and all had abnormally high temperature coefficients. The irregularities were attributed by Dearlove to the amalgam, the composition of which was found by him to exert a very decided influence on the e. m. f. Five cells set up with 12.5 per cent. amalgam in 1893 gave a temperature coefficient ranging between .003 and .007 per cent. per degree in the interval between 15° and 35°, and .007 to .010 per cent between 15° and 64°. Observations made while the cells were being brought back to room temperature, and others on cooling to 0°, showed that the results were influenced by marked hysteresis. Seven presumably similar cells, set up by Dr. Muirhead, were found by Dearlove to have a "temporary temperature coefficient" of .008 per cent. between 2.5° and 22°.

The generally accepted temperature formula for the Weston cell with excess of cadmium sulphate crystals, which alone will be considered in this paper, is based on a series of measurements by Jaeger and Wachsmuth[2], extending over a period of five days, during which the four cells employed were subjected to large and sudden temperature changes, no attempt being made to maintain the temperature constant for any considerable time. Besides the comparisons made at room temperature, 30 measurements in terms of two additional cells employed as reference standards are given, which may be summarized as follows:

On the first day two of the four cells were measured at 14.9°; on the following day the same cells were compared with each other at the same temperature. On the third day one cell was measured at 0° and two others at 9.0°, 9.1° and 9.6°. During the forenoon of the fourth day two cells at 1.7° and two at 12.6° and 12.8° were compared with the reference cells, while during the afternoon two sets of measurements were made at 25.3° and 25.9° on one cell of each lot. On the fifth day one cell at 1.5° and two at 20° were measured. Additional observations not given in the paper, and presumably check measurements at the above temperatures, are referred to in a foot-note.

[2] Wied. Ann., **59**, 575 (1896).
Elektrochn. Zeitschr., **15**, 507 (1894).

The cells in question were all made up with 14.3 per cent. amalgam, with which irregularities observed at lower temperatures have since been connected. The following formula was derived from *all* of the observations:

$$E_t = E_{20} - .000038(t - 20) - .00000065(t - 20)^2.$$

This formula has since been in general use. On account of irregularities observed between 0° and 5°, the authors limited its application to temperatures between 5° and 26°, and still later Jaeger[3] raised the lower limit to 10°.

These irregularities were first attributed by Kohnstamm and Cohen[4] to an inversion of cadmium sulphate similar to that observed in the case of zinc sulphate in the Clark cell, but it may be regarded as now established that no such inversion takes place between 0° and 60°. Irregularities have however been shown to be introduced by the employment of cadmium amalgams containing more than 15 per cent. by weight of cadmium. Jaeger[5] found that at room temperatures the e. m. f. of the Weston cell is almost independent of the composition of the amalgam employed, provided it contains between 5 and 14.3 per cent. cadmium. In the case of more concentrated amalgams the e. m. f. was found to be variable, the changes amounting to 1 millivolt for a 15.4 per cent. amalgam, 11 millivolts for a 20 per cent. amalgam, and 44 millivolts for amalgamated cadmium rods. Jaeger, therefore, recommended the use of a somewhat more dilute amalgam than that first employed, since its composition was too close to the limit at which irregularities were observed. No observations were, however, made by Jaeger at other than room temperatures. The subject has been investigated by Bijl[6] and Puschin[7], and it has been shown that cadmium amalgams consist, within certain temperature limits, of a liquid phase and a solid phase, the latter composed of mixed crystals of cadmium and mercury, having a composition depending on the temperature. With both phases coexistent the e. m. f. towards cadmium sulphate at a given temperature is, therefore, independent of the

[3] Zeitsch. Instrumentkunde, **20**, 317 (1900).
Ann. Phys., **4**, 123 (1901).

[4] Wied. Ann., **65**, 344 (1898).

[5] Wied. Ann., **65**, 106 (1901).

[6] Zeitsch. Phys. Chem., **41**, 641 (1902).

[7] Zeitsch. Anorg. Chem., **36**, 201 (1903).

relative amounts of the metals present as found by Jaeger, while in the absence of the liquid phase irregularities in behavior are found. The composition of the amalgam to be employed in the standard cell must therefore be such that both the liquid and solid phases will be present within the usual temperature range, a condition probably satisfied by the 12.5 per cent. amalgam employed at the Bureau of Standards and elsewhere.

A temperature coefficient more than twice as large as that obtained by Jaeger and Wachsmuth was found by Barnes[8], who measured three cells set up with 1 : 6 amalgam, two of which were filled with moist cadmium sulphate crystals instead of crystals and solution. Measurements were made between 0° and 40°, "allowing ample time at each interval for the establishment of a steady and uniform temperature." The observations at the various temperatures were completed in one day, the cells being kept at 0° during the night previous. The values obtained above 15° were fairly well represented by a linear coefficient of .0086 per cent. per degree, but under 15° Barnes states that no regularity can be said to exist, the difference between 0° and 15° being 2.1, 4.3 and 3.6 millivolts. From the observations made immediately before and after the above measurements, changes of + .11, — .35 and + .21 millivolts were found for the cells, indicating that trustworthy results are hardly to be expected after the relatively rapid temperature changes on account of hysteresis. Large differences were also found by Barnes in the values of four other cells rapidly brought from 15° to 0°.

A further study of all the Reichsanstalt cells with 1 : 6 amalgam was made by Jaeger[9] in 1896, but the results were not published until after the appearance of Barnes' paper. Thirty-four cells were measured in an oil bath at 0°, at which temperature 14 were found to differ from the values calculated by the formula of Jaeger and Wachsmuth by less than .02 per cent., while the observed values of the remaining 20 were from .02 to .23 per cent. (mean .09 per cent.) too high. The observations were made several hours after the bath had been cooled to 0°. In addition three of the cells, one belonging to the first group, and two of the second, were measured at temperatures between — 16°,

[8] Jour. Phys. Chem., **4**, 339 (1900).
[9] Ann. **4**, 123 (1901).

the freezing point of saturated cadmium sulphate solution, and 40°. The two "abnormal" cells showed maximum differences from the temperature formula of + 4.5 and + 3.2 millivolts, while the cell with "normal" behavior showed a maximum difference of — .57 millivolt (at — 11.5°). The observations extended over a period of two weeks, during which the cells were generally allowed to come to room temperature over night. After the first observation on each day, usually at room temperature, the cell was subjected to relatively large temperature changes. An inspection of the tables and the plotted results, particularly consecutive measurements on the same day, in which the temperature was changing slowly after a relatively large change, seems to indicate that the high values are due to hysteresis.

A very extensive series of observations between 0° and 30° was made by Jaeger and Lindeck[10] in 1899, with the object of checking the formula obtained by Jaeger and Wachsmuth. Fifty-six series of measurements were made on eight old cells with 14.3 per cent. amalgam and twelve new cells with 13 per cent. amalgam, together with five unsaturated Weston cells and five Clark cells with which we are not at present concerned. Six of the old Weston cells had already been classed by Jaeger as abnormal at lower temperatures, while the two others had apparently not been previously investigated at such temperatures. As might have been expected, these all showed marked irregularities, particularly at 0°, at which all the cells were kept for two periods of eight and eleven days, twenty-three series of measurements being made. The new cells, however, showed much smaller changes under these conditions. A second series of measurements was later made on five cells with 13 per cent. amalgam, set up at the same time as the twelve above referred to, and on two lots of twenty new cells set up with 12 and 13 per cent. amalgam. The results obtained at the Reichsanstalt will be discussed below in their relation to those found in the present investigation, particularly as the data obtained by Jaeger and Lindeck were not employed in the derivation of a temperature formula, being merely used for checking the previous work at the Reichsanstalt.

Two further series of measurements by Barnes and Lucas[11] on

[10] Zeitsch. Instk., **21**, 33 and 65 (1901).
Ann. Phys., **5**, 1 (1901).
[11] Jour. Phys. Chem., 8, 196 (1904).

four new "moist crystal" cells are summarized below. In the published tables only the uncorrected potentiometer readings are given so that the reductions were made on the assumption that the values of two portable cells of the Weston Electrical Instrument Company, measured at the same time, were the same for both sets of observations.

TABLE I.

Results of Barnes and Lucas.

Cells	Series	Temperature Range	Mean Temperature Coefficient		
			Observed	Range	Calculated
Cd 16	1	14.6°-27.9°	—0.0050%	0.0045-0.0057%	—0.0040%
17		14.6°-19.9°	0.0030	0.0024-0.0030	0.0035
18		19.9°-27.9°	0.0064	0.0064-0.0081	0.0043
19					
Cd 16	2	13 6°-29.5°	—0.0058	0 0057-0.0060	—0.0040
17		13.6°-18 7°	0.0024	0.0020-0.0028	0.0033
18		18.7°-29.5°	0.0075	0.0070-0.0078	0.0044

It will be seen that the results cannot be represented by a linear temperature coefficient, that the differences in temperature coefficient between the individual cells are large, and that the values for the lower range are *smaller* than those called for by the generally accepted temperature formula. The results can, therefore, not be regarded as confirming the previous work of Barnes as to the temperature coefficient being linear, nor do they establish the opinion expressed by Barnes that the differences in results are due to the greater rapidity with which saturation equilibrium is established in the case of the "moist crystal" cells in comparison with cells of the usual construction.

Smith[12], at the English National Physical Laboratory, has recently found, as the result of measurements on six selected cells between 10° and 30°, the formula:

$$E_t = E_{17} - .0000345(t - 17) - .00000066(t - 17)^2.$$

The temperature was changed at the rate of 1° per hour and maintained constant by means of a thermo-regulator at least one hour

[12] Phil. Trans. Roy. Soc., 207, 411 (1908).

before the measurements were made, the cycle of temperatures being repeated three times. The data on which the formula is based are not published, but judging from the results obtained at the Bureau on cells obtained by exchange from the National Physical Laboratory, some hysteresis may be expected under the above conditions. On account of the close agreement, in the range covered, of Smith's formula with that of the Reichsanstalt, the universal adoption of the latter is recommended by him.

THE PRESENT INVESTIGATION.

The Cells: In the present investigation it was thought desirable to include a large number of cells, so as to determine whether any differences in the temperature coefficient are introduced by variations in the methods of preparation and purification of the materials. Altogether 200 cells were studied, including nearly all those previously reported on,[13] a number of exchange cells obtained from other investigators, and a considerable number of other cells set up at the Bureau to determine the influence of variations in the specifications which might possibly affect the e. m. f.

The Comparing Baths: The cells were contained in two automatically regulated petroleum baths, each provided with an efficient stirrer, a thermo-regulator sensitive to within .01° C., resistance coils for electric heating, and coils for water circulation for temperatures below that of the room. As described in the article referred to, the cells were mounted in such a way as to be free from direct influence of the heating or cooling coils. The oil in which the cells were immersed covered them to a depth of several centimeters.

The Temperature Cycle: The measurements were made at every 5° for a complete cycle from 0° to 40°, beginning and ending at 25°, the lower temperatures being taken first, and a smaller cycle from 15° to 25°. As it was deemed desirable to repeat the 0° measurements with ascending temperatures, both baths were maintained at a temperature of approximately — 4° for 24 hours between the two series of observations made at 0°. The regulator was set so that the temperature at which the baths regulated was within ± .02° of the temperature desired, except for 10 sets in bath 1 and 4 sets in bath 2, so that, by applying a slight

[13] Wolff and Waters, Bull. Bur. Stands., 4, 1 (1907). (Reprint No. 70.)

correction, the values observed could be reduced to the temperatures decided upon, thus making possible the application of at least squares formula to the reduction of the results.

Regulation: The temperature of the baths was maintained constant well within .02° C. for at least 40 hours at each temperature ascending and descending.

No difficulty was, of course, experienced in regulating the baths at temperatures above that of the room (about 23°) but at 20° and 15° great difficulty was at first found, mainly on account of the cooling coils of both baths being in parallel. In the first measurements at these temperatures, the cooling was effected by a very slow stream of tap water which had been passed through a lead coil surrounded by crushed ice. (The use of ice even for these temperatures was made necessary on account of the temperature of the tap water rising above 20° during the night.) The difficulty was traced to the separation of air bubbles from the water, which, collecting in the cooling coils, gradually obstructed the circulation and thus disturbed the regulation. Various schemes were tried, but the most satisfactory method consisted in pumping water from a tank maintained several degrees below the temperature at which the baths were to be regulated. For this purpose a slow flow of ice water into the tank sufficed, the level being maintained by means of an overflow. A direct circulation of ice water was employed for the auxiliary cooling at 10°, while the low temperatures, 5°, 0° and —4°, were obtained by circulating a brine solution of suitable concentration, the brine being kept approximately at its freezing point by means of a coil in the same tank through which much cooler brine was circulated at a desired rate by the aid of a by pass. In the few cases of defective regulation, occasioned by the separation of air bubbles, broken belts, etc., a new start was made and the cells were maintained at the desired temperatures for at least 40 hours longer.

Method of Observation: As the apparatus and method of observation have already been fully described,[14] only an outline will be here given. Each of the 200 cells was measured in opposition to a particular cell in a separate bath maintained at 25°. The latter was compared in a similar manner with 14 cells,

[14] Wolff and Waters, Bull. Bur. Stands., 4, 39 (1907).

composing two sets of seven, in the same bath with it and to which all the results were reduced. In addition, the seven cells of one of the reference sets, connected in series, were directly compared by the opposition method with five sets of seven cells in each of the two baths. The slight differences found by the two methods, averaging ± 2 microvolts per cell, exceeded 3 microvolts in only ten series.

Altogether 58 observations were made on each of the 200 cells, and 19 others kept at 25°, in completing the two cycles. At each step at least two series of measurements were made, the first on the day after the temperature was changed and the last after the cells had been at constant temperature at least 40 hours.

Including the series measurements, over 12,000 separate observations were therefore made, about 3,500 being employed in the calculations for the cells tabulated below.

Temperature Measurements: On account of the relatively small temperature coefficient of the Weston cell, all temperature measurements were made with sufficient accuracy by means of mercurial thermometers, graduated to tenths of a degree, for which the corrections were determined to .01° by another Division of the Bureau.

Reduction of Results: In working up the results, three corrections were applied to each observation. The first to reduce all results to a common basis, the mean value of the reference cells, the second to allow for the very slight temperature differences of the baths from their nominal values, and the third, one-half the mean difference found by comparing the cells separately and in sets of seven in series. The two latter corrections rarely exceeded 2 microvolts.

A preliminary temperature formula was first calculated by the least squares method from the means of all the observations on 10 cells selected on account of their small hysteresis as indicated by the agreement of the observations with ascending and descending temperatures. Although these values agreed within 5 microvolts of each other, it was found that they could not be represented as well as might be expected by a quadratic formula. A three term formula was, therefore, tried which was found to

give residuals of ± 2 microvolts. With the approximate temperature formula thus found,

$$E_t = E_{20} - .0000406(t - 20) - .000000939(t - 20)^2 + .000000009(t - 20)^3$$

the residuals for each cell at each temperature could be computed, and from these, corrections to the above coefficients for the individual cells were obtained. The residuals found at each temperature for the ten cells by the employment of the corrected coefficients thus obtained, agreed with each other to within ± 2 microvolts. This, with the close agreement of the third term coefficients of the individual cells, fully justifies the use of a three term formula.

The results for a considerable number of cells were worked up by taking into account all the observations made, but an inspection of the values obtained for the cells which gave, for the same temperature, differences with ascending and descending temperatures, showed a steady approach to the same value. It was therefore thought best to reject all but the last measurements of each series at the same temperature. These measurements, which were made at least 40 hours after the temperature was changed by 5°, were given equal weight in computing the corrections to the coefficients of the trial formula.

In the following tables in which the results were summarized, the cells are grouped according to the method of preparation or treatment of the mercurous sulphate employed in the cell[15] Column 1 gives the number of the cell; column 2 the designation of the sample, the letter indicating the method employed; column 3, the mean of the total range in value of each cell at each temperature, all observations being included; column 4, the mean range of the values found in the last measurements of each set at each temperature; column 5, the maximum range corresponding to column 4, and columns 6, 7 and 8 corrections to be applied algebraically to the coefficients of the trial formula.

DISCUSSION OF THE RESULTS.

In the tables the results for 178 of the 200 cells are given. The 22 omitted are made up of 7 exchange cells, 5 cells containing oil admitted through defective seals, 8 cells of a series set

[15] Bull. Bur. Stands., 4, 41 (1907).

up to determine possible electromotive differences with samples of cadmium sulphate obtained from different sources and purified by different methods, together with 2 cells set up with white mercurous sulphate paste which had been employed in special cells[16], constructed to make possible a study of the influence of a thorough and continuous mixing of the ingredients of the paste by rotation of the cell about its axis. In all these cases the differences between the values obtained with ascending and descending temperatures are very large and irregular, and in addition the majority exhibited abnormal values before beginning the temperature cycle. The results seem to indicate a lag in the establishment of concentration equilibrium of the mercury ions, as abnormally high values are obtained at lower temperatures. This behavior is particularly marked in the cells set up to deter-

TABLE II.

Electrolytic Mercurous Sulphate Made with Old Apparatus.

Cell	Mercurous Sulphate	Mean Range in Microvolts		Maximum Range in Microvolts	Corrections to Coefficients in Microvolts		
		All Observations at Each Temperature	Last Observations at Each Temperature	Last Observations at Each Temperature	△ Alpha	△ Beta	△ Gamma
*75	a1	75	37.2	100	+8.16	—0.032	—0.0042
*76	a4	23	8.3	17	+1.69	—0.021	—0.0003
77	a¹4	7	2.6	7	—0.35	—0.049	+0.0020
*64	a5	50	22.5	66	+4.37	—0.042	—0.0002
*65	a6	27	12.8	30	+2.12	—0.021	+0.0002
*40	a7	127	63.3	145	+19.82	—0.458	—0.0217
*8a	a7	99	58.3	100	+6.29	+0.067	—0.0056
*66	a¹7	33	13.7	39	+2.44	—0.010	+0.0002
*41	a8	84	38.6	82	+5.42	—0.074	+0.0002
*9a	a8	42	26.2	48	+2.34	+0.062	—0.0046
67	a¹8	20	8.5	20	+1.46	0.000	—0.0032
*42	a9	52	35.0	46	+3.50	+0.013	—0.0019
11a	a9	11	2.4	4	+0.94	—0.013	—0.0006
68	a10	21	9.5	20	+1.44	—0.011	—0.0001
70	a¹10	6	4.2	9	—0.41	+0.009	0.0000
71	a11	6	3.2	9	—0.29	+0.020	—0.0008
*72	a¹11	28	12.9	25	+1.77	+0.024	0.0000
73	a12	7	3.0	5	+0.12	+0.004	0.0000
74	a13	14	10.0	20	—0.11	+0.017	—0.0001
110	a13	7	2.8	10	—0.30	+0.015	—0.0006
112	a13	14	9.6	11	+0.06	+0.005	—0.0008
113	a13	4	2.0	4	—0.50	+0.011	—0.0004

*Excluded in taking means.

[16] Wolff and Waters, Bull. Bur. Stands., 4, 81 (1907).

Table III.

Electrolytic Mercurous Sulphate Made with New Apparatus.

Cell	Mercurous Sulphate	Mean Range in Microvolts		Maximum Range in Microvolts	Corrections to Coefficients in Microvolts		
		All Observations at Each Temperature	Last Observations at Each Temperature	Last Observations at Each Temperature	Δ Alpha	Δ Beta	Δ Gamma
*26	b1	30	12.9	25	+1.59	—0.034	+0.0004
51	b1	9	5.2	10	+0.30	—0.004	—0.0003
27	b2	4	1.5	3	+0.02	—0.003	—0.0002
52	b2	15	9.2	22	+0.99	—0.034	—0.0007
*28	b3	28	11.1	26	+1.85	—0.019	—0.0002
61	b4	19	6.9	21	—0.10	+0.018	—0.0004
62	b5	11	7.4	16	+0.10	—0.001	—0.0008
63	b6	10	5.6	11	—0.05	+0.004	0.0000
29	b7	17	6.9	12	+0.67	—0.009	0.0000
3a	b7	8	3.2	7	—0.21	+0.019	—0.0004
167	b7	5	2.2	7	—0.17	+0.014	—0.0012
168	b7	8	3.6	10	+0.07	—0.007	—0.0002
168a	b7	11	6.6	15	—0.29	+0.023	—0.0011
30	b8	23	7.4	12	+1.26	+0.001	—0.0001
*193	b8	42	22.9	38	+2.29	+0.005	0.0000
46	b8	9	3.6	5	—1.15	+0.015	+0.0042
46a	b8	6	3.2	8	—0.16	+0.007	—0.0001
*46b	b8	30	15.8	35	+0.94	+0.097	—0.0059
31	b9	11	5.8	10	+0.67	—0.018	—0.0004
47	b9	6	2.6	4	—0.24	—0.005	+0.0003
32	b10	3	1.8	5	+0.68	+0.003	+0.0002
4a	b10	9	5.1	11	—0.17	+0.027	—0.0015
33	b11	11	3.8	9	+0.40	0.000	—0.0002
48	b11	14	6.3	9	+0.42	—0.022	—0.0006
34	b12	11	5.1	8	+0.81	—0.021	+0.0002
49	b12	15	9.2	19	+0.33	0.000	—0.0002
6a	b13	4	2.2	5	—0.39	+0.010	—0.0002
176	b13	12	4.5	12	—0.21	+0.013	—0.0004
151	b14	6	2.6	8	—0.45	+0.009	0.0000
152	b14	6	2.1	4	—0.46	+0.007	—0.0001
153	b14	4	2.6	7	—0.33	+0.012	—0.0004
154	b14	3	1.1	2	0.00	+0.009	+0.0002
155	b14	4	1.7	6	—0.03	+0.012	—0.0001
156	b14	4	2.3	6	—0.12	+0.011	—0.0002
164	b14	10	3.2	9	—0.24	+0.014	+0.0002
†165	b14	4	2.5	8	—0.47	+0.019	—0.0005
†166	b14	10	5.2	10	—0.14	+0.022	—0.0012
111	b14	8	4.1	13	—0.36	+0.017	—0.0006
113	b14	7	2.5	8	—0.24	+0.007	—0.0002
171	b14	5	2.1	5	—0.58	+0.006	0.0000
172	b14	5	2.0	5	—0.49	+0.009	—0.0005
37	b15	5	2.5	8	—0.40	+0.005	+0.0001
*15a	b16	25	12.5	35	+0.91	+0.055	—0.0051
69	b17	8	3.8	11	—0.36	+0.012	—0.0003
59	b18	7	2.6	9	+0.10	+0.011	—0.0002
60	b19	8	4.2	13	—0.04	+0.009	—0.0002
*50	b20	34	13.3	46	+3.12	—0.011	—0.0012
*53	b21	18	11.2	26	+0.40	+0.007	—0.0012
54	b22	12	7.8	13	+0.01	+0.006	—0.0007
55	b23	9	5.6	12	—0.31	+0.022	—0.0008
56	b24	5	2.4	6	—0.30	+0.023	—0.0009
57	b25	8	3.1	8	—0.32	+0.021	—0.0010
178	b26	8	3.3	12	—0.19	+0.037	—0.0024
*P9	b26	32	12.1	39	+0.23	+0.081	—0.0035
*P11	b26	99	20.9	125	+0.48	+0.182	—0.0071
*P12	b26	23	7.1	30	+0.52	+0.074	—0.0054
179	b27	7	4.1	17	—0.33	+0.035	—0.0022
187	b27	6	2.4	5	—0.26	+0.013	—0.0006
188	b27	7	2.6	5	—0.21	+0.036	—0.0024
180	b28	9	2.9	8	+0.06	+0.051	—0.0036
190	b29	11	5.5	9	+0.06	—0.001	—0.0006
191	b30	9	4.9	11	—0.15	+0.029	—0.0018
192	b31	10	3.0	7	—0.08	+0.032	—0.0019

* Excluded in taking means. † Clear Crystal Cells.

Table IV.

Chemically Prepared Mercurous Sulphate.

Cell	Mercurous Sulphate	Mean Range in Microvolts		Maximum Range in Microvolts	Corrections to Coefficients in Microvolts		
		All Observations at Each Temperature	Last Observations at Each Temperature	Last Observations at Each Temperature	△ Alpha	△ Beta	△ Gamma
86	c	3	1.3	3	−0.31	+0.003	−0.0001
99	d1	8	4.3	8	+0.60	−0 025	−0.0001
99a	d1	10	5.9	8	+0.29	0.000	−0.0003
84	d2	7	4.4	11	−0.52	+0.007	+0.0003
84a	d2	4	1.9	5	−0.38	+0.006	+0.0002
*43	e1	30	13.5	31	+0.94	+0.047	−0.0034
1a	e1	20	8.8	16	+0.97	+0.012	−0.0016
157	e1	15	7.8	20	+0.54	+0.072	−0.0050
158	e1	8	2.6	8	−0.26	+0.020	−0.0010
160	e1	9	6.2	25	−0.14	+0.006	−0.0004
161	e1	5	2.9	11	−0.36	+0.007	−0.0006
162	e1	5	1.7	8	−0.26	+0.017	−0.0010
103	e2	7	3.4	6	−0.54	+0.020	−0.0000
2a	e2	17	9.8	17	+0.03	−0.009	+0.0004
44	e3	14	5.8	11	+0.34	+0.048	−0.0037
104	e3	4	2.1	9	−0.48	+0.014	−0.0004
105	e4	5.7	2.6	4.0	−0.10	+0.103	−0.0006
106	e5	6.7	2.9	8.0	−0.09	+0.009	−0.0005
106a	e5	4.8	1.2	3.0	−0.26	+0.015	−0.0006
107	e6	6.2	3.1	9.0	+0.38	+0.102	−0.0004
98	f1	10.1	2.5	8.0	+0.07	+0.041	−0.0029
97	f2	3.9	1.1	2.0	−0.06	+0.007	−0.0007
*100	g1	55.8	23.6	53.0	+5.24	−0.025	−0.0019
*100a	g1	68.4	37.6	66.0	+3.49	−0.017	−0.0004
*101a	g2	126.7	90.6	160.0	+4.98	−0.015	−0.0028
*163	g3	39.6	16.8	29.0	+3.21	−0.039	−0.0031
*95	h1	40.7	21.1	46.0	+2.06	+0.043	−0.0050
*96	h2	48.7	27.2	43.0	+4.71	+0.051	−0.0087
85	h3	4.6	2.1	5.0	−0.34	+0.001	−0.0002

*Excluded in taking means.

Table V.

Specially Treated Commercial Samples of Mercurous Sulphate.

Cell	Mercurous Sulphate	Mean Range in Microvolts		Maximum Range in Microvolts	Correcrions to Coefficients in Microvolts		
		All Observations at Each Temperature	Last Observations at Each Temperature	Last Observations at Each Temperature	△ Alpha	△ Beta	△ Gamma
93	i1	14	5.5	8	+0.87	+0.006	−0.0015
94	i2	5	1.4	3	−0.04	−0.001	−0.0003
78	k1	4	2.3	7	+0.33	+0.017	−0.0001
79	k2	4	1.6	4	+0.09	+0.016	−0.0002
80	k3	4	1.6	4	−0.31	+0.008	−0.0004
81	k4	6	2.2	5	−0.01	+0.016	−0.0002
82	k5	7	3.9	8	+0.06	+0.003	−0.0005
108	l1	7	3.1	8	+0.87	+0.015	−0.0006
116	l2	16	7.1	2.4	+0.38	+0.005	−0.0006
109	l3	6	2.2	4	+1.00	+0.002	−0.0001
114	l4	6	2.8	5	+0.24	0.000	−0.0006
115	l5	5	1.7	4	+1.08	+0.010	−0.0009
117	m1	8.3	5.1	8.0	+1.50	+0.006	−0.0014
119	m2	7.8	3.2	9.0	+0.15	+0.009	−0.0008
118	m3	7.7	4.0	25.0	+0.37	+0.004	−0.0012
120	m4	8.9	4.0	16.0	+0 04	+0.014	−0.0013
90	n4	6.6	2.2	6.0	+0.43	+0.020	−0.0005
91	n5	5.8	1.8	3.0	+0.73	−0.022	−0.0004
92	n6	6.4	2.1	8.0	+0.18	−0.008	0.0000

Table VI.

Exchange Samples of Mercurous Sulphate.

Cell	Mercurous Sulphate	Mean Range in Microvolts		Maximum Range in Microvolts	Corrections to Coefficients in Microvolts		
		All Observations at Each Temperature	Last Observations at Each Temperature	Last Observations at Each Temperature	△ Alpha	△ Beta	△ Gamma
39	Hulett I	15	6.2	12	+0.14	+0.003	—0.0001
141a	Hulett II	5	2.6	6	—0.30	+0.014	—0.0005
142	"	7	3.2	7	—0.05	+0.005	—0.0008
143	"	4	2.4	9	—0.31	—0.002	0.0000
144	"	5	3.6	14	—0.20	—0.006	+0.0001
145	"	5	3.0	4	—0.18	+0.005	—0.0004
146	"	11	6.2	19	—0.12	+0.021	—0.0011
147	"	5	1.9	6	—0.30	+0.005	—0.0004
148	"	8	3.5	7	+0.16	—0.003	—0.0007
149	"	6	2.7	5	+0.08	0.000	—0.0007
150	"	5	1.6	5	—0.44	—0.029	—0.0009
†169	"	5	2.2	10	—0.08	—0.004	0.0000
†170	"	11	7.4	18	0.00	+0.033	—0.0012
*189	"	23	13.3	28	+0.94	+0.065	—0.0048

* Excluded in taking means.

† Clear Crystal Cells.

Table VII.

Exchange Cells.

Cell		Mean Range in Microvolts		Maximum Range in Microvolts	Corrections to Coefficients in Microvolts		
		All Observations at Each Temperature	Last Observations at Each Temperature	Last Observations at Each Temperature	△ Alpha	△ Beta	△ Gamma
O2	P. T. R.	13	7.8	12	+1.85	—0.054	+0.0004
*4	L. C. E.	92	37.6	108	—0.28	—0.153	+0.0036
*6	L. C. E.	94	36.3	86	+1.16	—0.175	+0.0055
*H26	N. P. L.	40	25.0	46	+1.23	—0.050	+0.0011
*C19	N. P. L.	147	82.5	214	+3.05	—0.400	+0.0146
P53	N. P. L.	19	8.0	22	—0.50	—0.045	+0.0008
*P54	N. P. L.	48	26.5	63	+1.13	—0.016	+0.0034
K11	N. P. L.	4	1.7	5	0.00	+0.012	—0.0006
K15	N. P. L.	4	1.5	5	—0.06	+0.010	—0.0003
*HB9	N. P. L.	46	11.3	28	+1.85	—0.065	+0.0033
57	Wold	9	2.4	5	+0.01	+0.009	+0.0003
†*O4	Hulett	43	23.9	82	—2.43	+0.021	+0.0037
†A3	Hulett	14	8.5	13	+0.10	+0.015	—0.0008
†*A52	Hulett	26	12.3	28	+1.94	—0.011	—0.0003
†C1	Guthe	25	9.5	20	—0.48	+0.028	—0.0003
†*5	Carhart	19	10.6	57	+0.29	+0.044	—0.0022
†*8	Carhart	39	23.6	36	+2.13	—0.033	+0.0003
1	Strong	21	9.1	15	+0.48	+0.013	+0.0002
*2	Strong	31	12.8	29	+1.27	+0.017	—0.0001
3	Strong	15	5.7	14	+0.10	+0.022	+0.0002

* Excluded in taking means.

† Clear Crystal Cells.

TABLE VIII.

Cells Set up with Different Samples of Cadmium Sulphate.

Cell	Mercurous Sulphate	Mean Range in Microvolts		Maximum Range in Microvolts	Corrections to Coefficients in Microvolts		
		All Observations at Each Temperature	Last Observations at Each Temperature	Last Observations at Each Temperature	△ Alpha	△ Beta	△ Gamma
121	b15	6	2.6	9	—0.33	+0.006	—0.0002
122	b15	5	2.1	7	—0.48	+0.016	—0.0005
123	b15	4	2.1	6	—0.42	+0.011	—0.0002
124	b15	10	5.4	11	—0.05	0.000	—0.0008
125	b15	11	5.6	14	+0.39	—0.002	—0.0012
126	b15	6	1.9	4	+0.68	+0.016	—0.0010
127	b15	7	4.4	10	—0.35	+0.012	—0.0006
128	b15	8	4.0	9	—0.42	+0.021	—0.0005
133	b15	10	5.5	13	+0.36	—0.005	—0.0001
*136	b15	33	16.2	44	+0.61	—0.101	—0.0007
138	b15	14	8.3	22	+0.46	—0.010	—0.0012

*Excluded in taking means.

mine differences in the electromotive properties of different samples of cadmium sulphate, in which, in order to eliminate differences arising from the mercurous sulphate, relatively small quantities had to be employed, owing to the supply of the particular sample of mercurous sulphate being limited. The paste, in most cases, therefore, contained a relatively large excess of cadmium sulphate crystals. In two of the exchange cells, set up at the University of Wisconsin, and which also exhibited abnormal and variable values before beginning the temperature cycle, there does not appear to be an excess of cadmium sulphate crystals in the paste. Among the other exchange cells excluded are one of the two obtained from the Reichsanstalt, in both of which the paste seems to have been disturbed in transit, two cells obtained from the National Physical Laboratory in 1904, and two set up by Prof. Hulett, in both of which oil was admitted through defective seals. All these cells exhibited abnormal values, particular attention being called to the behavior of F-7, set up by Prof. Hulett in 1904, and which belonged to the series, the behavior of which led him to suspect that the chemical system of the Weston cell is in unstable equilibrium.

In view of the unmistakable hysteresis found in some of the other cells for which the data are tabulated above, not all should

be included in calculating the mean values of the coefficients of the temperature formula. An arbitrary criterion for rejection has, therefore, been decided upon, those cells being excluded in which the mean maximum difference with ascending and descending temperatures, taking the last measurements of each set at each temperature, exceeded 10 and 25 microvolts respectively. (Columns 4 and 5.) Even on this basis 137 cells, over two-thirds of the whole number taken, pass inspection. Among those excluded are 11 of the 22 cells given in Table II, in all of which relatively coarse grained white samples of mercurous sulphate were employed; 10, including 3 portables of special construction, of the 63 of Table III, all set up with gray samples of electrolytic mercurous sulphate; 7 of the 29 cells of Table IV, nearly all set up with coarse grained white samples of chemically prepared mercurous sulphate; 1 of the 14 cells set up with exchange samples of mercurous sulphate; 11 of the 20 exchange cells and 1 of the 11 cells of Table VIII.

The following table shows the agreement of the mean corrections to the coefficients of the trial formula, corresponding to the same grouping as in Tables II to VIII inclusive, excluding the 41 cells just referred to. The values given in the last line are the mean corrections for the 137 cells, the corrections for each cell being assumed to have equal weight.

TABLE IX.

Mean Corrections to Coefficients of Trial Formula.

Table	Number of Cells	Mean Correction to Coefficients in Microvolts		
		△ Alpha	△ Beta	△ Gamma
II	11	+0.19	+0.001	—0.0004
III	53	—0 07	+0.010	—0.0005
IV	22	—0.04	+0.022	—0.0009
V	19	+0.42	+0.006	—0.0006
VI	13	—0.12	+0.004	—0.0005
VII	9	+0.17	+0 001	+0.0000
VIII	10	—0.02	+0.006	—0.0006
II—VIII	137	+0.04	+0.009	—0.0006

The agreement of mean corrections for the separate groups is excellent. Particular attention should be called to the results for the exchange cells (Table VII) which do not differ appreciably from the rest. Applying the mean corrections of the 137 cells to the trial formula we obtain the equation:

$$E_t = E_{20} - .00004064(t - 20) - .000000949(t - 20)^2 + .0000000096(t - 20)^3$$

by which the results are best represented.

Since all the cells of the Bureau of Standards were set up with 12.5 per cent. amalgam, it seems probable that the number of hysteresis observed in almost one-third of the whole number taken lies elsewhere. The agreement of the cells set up with large crystals of cadmium sulphate (marked † in the tables) with the remainder in which finely crushed cadmium sulphate crystals were employed, indicates that the irregularities are connected with the paste limb. This conclusion is strengthened by the behavior of the cells in which scant quantities of mercurous sulphate were employed in making up the paste. A further study of the abnormal cells will be undertaken with the object of establishing definitely the cause of their irregularities by an analysis of their ingredients, by setting up new cells to verify the conclusions which may thus be reached and by a redetermination of the temperature coefficient and behavior of amalgams, particularly at lower temperatures.

After making an analysis of the results here given, it seemed probable that the cells exhibiting hysteresis should also have shown abnormal initial values, as the laboratory temperature was generally higher than 25°, the temperature of the comparing baths. An examination was, therefore, made of the observations on the particular cells immediately after they were set up, and in nearly every case evidence of hysteresis was indeed found. This was commented on in the paper on the Clark and Weston cell frequently referred to, where attention was called to the fact that such cells tended to approach normal values. The exceptions to this rule are nearly all found in the cells of Table V, set up with commercial samples of mercurous sulphate treated with sulphuric acid under various conditions, some of which exhibited relatively high initial values which, however, have persisted without appreciable change. Not one of these cells shows appreciable

hysteresis, indicating that the high values are probably due to residual impurities.

TEMPERATURE OF MAXIMUM ELECTROMOTIVE FORCE.

In making the first sets of measurements at 5° and 0° it was found that the temperature coefficient unmistakably changed sign between these limits, which was verified by the subsequent observations with ascending temperatures.

The differentiation of the corrected temperature formula gave + 3° as the temperature of maximum electromotive force and zero temperature coefficient. Since this corresponds approximately to the temperature of saturation of the cadmium sulphate solution employed in the portable cells of the Weston Electrical Instrument Company, which have a practically negligible temperature coefficient, the solublity curve of cadmium sulphate was computed by the least squares method from the data of Mylius and Funk.[17] The observations, while not as concordant as might have been desired, ranged, from — 10° to + 60° and led to a formula giving a minimum soluble at + 1°. The very close agreement of these values has suggested further experimental work, which, it is hoped, can shortly be undertaken.

RESULTS OBTAINED BY OTHER INVESTIGATORS.

A brief outline of previous work on this subject has been given above, and it therefore only remains to compare the results obtained with those found in this investigation. Since the results obtained by Dearlove, Barnes, and Barnes and Lucas are quite irregular, and indicate the existence of large hysteresis effects, as has been pointed out above, this discussion will be confined to a comparison of the results obtained at the Reichsanstalt and at the Bureau of Standards.

The original measurements by Jaeger and Wachsmuth[18], upon which the generally accepted formula is based, were therefore reduced by the author, and it was found that if the observations at 0°, 1.5° and 1.7° were excluded the average deviation of the measurements from the new formula amount to ± 13 microvolts as compared with ± 8 microvolts by the generally accepted for-

[17] Ber. **30**, 824 (1897).
[18] Wied. Ann., **59**, 575 (1896).

mula. When it is recalled that the results of Jaeger and Wachsmuth were obtained from a relatively small number of measurements on four cells, set up with 1 : 6 amalgam, and that no attempt was made to maintain the temperature at a constant value for any length of time, the agreement is quite remarkable. The exclusion of the observations at the lower temperatures, at which the differences from the proposed formula are from 100 to 200 microvolts, is fully justified by Jaeger's admission of the existence of irregularities below 10° for the 1 : 6 amalgam.

As pointed out in the introduction to this paper, the results obtained by Jaeger in 1898, also apply to cells with amalgam of the same composition, and further establish the existence of irregularities at lower temperatures. The differences between individual cells of the same lot indicates, however, that the abnormal values may not be entirely due to the 1 : 6 amalgam.

The results obtained by Jaeger and Lindeck[19-20], in 1899-1901, have also been carefully worked over. No particular attention was paid to the eight old cells with 1 : 6 amalgam, six of which were among those previously reported as abnormal. The 56 series of measurements on twelve new cells with 13 per cent. amalgam were first tabulated. The two series at 0° extending over two periods of 8 and 11 days, show relatively large differences between the individual cells, as well as a not inconsiderable hysteresis. Instead of taking the mean of all such measurements, the mean of the last three in each series was taken. Series 15 and 54 were also excluded on account of relatively sudden temperature changes. The observations were otherwise grouped in the same manner as was done by Jaeger and Lindeck, and from these the mean values of the twelve cells at twelve temperatures in the range of 0° to 30° were obtained. The mean deviation from the Reichsanstalt formula was found to be ± 40 microvolts, while the mean deviation from the formula here proposed amounts to ± 20 microvolts. This suggested the desirability of computing a temperature formula from the Reichsanstalt results. It was found that the mean values of the twelve cells, the observations grouped as above, could best be expressed by the formula:

[19] Ann. Phys., **5**, 1 (1901).
[20] Zeitschr. Instk., **21**, 33-65 (1901).

$$E_t = E_{20} - .00003988(t - 20) - .000000941(t - 20)^2 + .0000000146(t - 20)^3$$

with a mean residual of $\pm$ 10 microvolts. In addition, the coefficients are in excellent agreement with those of the temperature formula proposed.

The result of further measurement made on five cells set up up at the same time and with the same material as the twelve to which the above results apply, together with those obtained with two new lots of 20 each set up with respectively 12 per cent. and 13 per cent. amalgams, are given in Table X. The cells were only measured at 0°, at which they were kept for several days, and at room temperatures. The b and β groups were freshly set up and changed considerably between the measurements at room temperatures, made before and after the observations at 0°, so that the differences between 0° and 20° were calculated on the assumption that the rate of change was uniform in the interval.

TABLE X.

Summary of Results—Jaeger and Lindeck.

Cells	Number	Per Cent. Amalgam	Mean Difference in Microvolts 0°-20°
a1-a5 a11-a17	12	13	318
a6-a10	5	13	230
b1-b15	15	13	433
b16-b20	5	13	379
β1-β5	5	12	345
β6-β20	15	12	355
All	57	—	358

The agreement of the individual cells as well as the separate groups is not entirely satisfactory and hardly establishes the existence of a difference in the mean temperature coefficient between 0° and 20°, arising from the employment of 12 and 13 per cent. amalgams. The mean difference in value between 0° and 20° for the 137 cells, all set up with 12.5 per cent amalgam, on which the proposed formula is based, is 356 microvolts, while that given by the formula of Jaeger and Wachsmuth is 500 microvolts, so that it may safely be concluded that the heretofore

accepted formula cannot be safely applied beyond the limits, 10°-30°, indicated by Jaeger.

In Table XI are given the differences in e. m. f. calculated by the various formula, for every 5° from 0° to 40°, in terms of the value at 20° taken as standard.

TABLE XI.

Differences in Microvolts from 20° Value by the Various Formulae.

Temp.	Jaeger and Wachsmuth	Jaeger and Lindeck*	Smith	Wolff
0	+500	+304	+505	+357
5	+424	+337	+428	+364
10	+315	+290	+319	+302
15	+174	+174	+176	+178
20	0	0	0	0
25	—206	—221	—209	—226
30	—445	—478	—451	—492
35	—716	—661	—725	—690
40	—1020	—1057	—1033	—1115

*Computed by Author.

From the table it will be seen that a very good agreement exists between 10° and 30°. In work of the highest precision, however, the differences, amounting to 20 microvolts in the interval 20° to 25°, between the generally accepted formula and that proposed, may have to be taken into account.

SUMMMARY OF CONCLUSIONS.

From the results obtained in this investigation the following conclusions may be drawn:

1. That Weston cells can be set up which exhibit extremely little hysteresis in the range 0° to 40°, even when subjected to large and rapid temperature variations.

2. That such cells will maintain their values under prolonged heating or cooling.

3. That the relation between e. m. f. and temperature is best represented by the formula:

$$E^t = E_{20} - .00004064(t - 20) - .000000948(t - 20)^2 + .0000000096(t - 20)^3$$

4. That no indications were found of differences arising

from the methods of preparation of the mercurous sulphate employed.

5. That the results of Jaeger and Lindeck on cells with 12 and 13 per cent. amalgams are in better agreement with the formula given above than with the generally accepted temperature formula, which, however, agrees fairly well with the former between 10° and 30° C.

6. That some of the cells showed marked and persistent hysteresis, particularly at lower temperatures for which the values are in general greater than those corresponding to the formula above given.

7. That the majority of cells in which hysteresis was found were set up with relatively coarse grained white samples of mercurous sulphate.

8. That a similar behavior was found in most of the cells having abnormal values at room temperatures, and in cells in which oil had been admitted through defective seals.

9. That nearly all the cells exhibiting abnormal initial values showed evidence of decided hysteresis.

10. That according to the above formula the e. m. f. of the Weston cell has a maximum value at 3°, corresponding approximately to the temperature of minimum solubility of cadmium sulphate, and to the saturation temperature of the cadmium sulphate solution employed in the portable cells of the Weston Company for which the temperature coefficient is almost negligible.

The author wishes to acknowledge the valuable assistance given him by Mr. M. P. Shoemaker and Mr. J. H. Dellinger in making about half of the observations, and to Mr. Shoemaker for the careful regulation of the baths and for his painstaking labors in the computation of the results.

DISCUSSION.

Professor Carhart: I should like to ask Dr. Wolff some questions. Dr. Wolff says he finds some hysteresis through this wide range of temperature from zero to forty degrees. He did not tell us which is too high and which too low, the values with rising temperature or with falling.

DR. WOLFF: The cells exhibiting hysteresis are generally closer to normal values with ascending temperatures than with descending temperatures.

PROFESSOR CARHART: Going down in temperature the values are too low or too high?

DR. WOLFF: Too low while the temperature was being lowered. After regulation at the new temperature, nearly all the cells exhibiting hysteresis gave high values.

PROFESSOR CARHART: The values are too low going down from high temperatures? That would indicate to my mind a failure to crystallize fast enough. Then I would ask how long a period was taken in finishing any one curve?

DR. WOLFF: The cells were maintained at constant temperature, within one or two hundredths of a degree for at least forty-eight hours.

PROF. CARHART: For each temperature?

DR. WOLFF: For each temperature. Even after that length of time, forty-eight hours, there was still residual hysteresis in some of the cells.

PROF. CARHART: I ask if Dr. Wolff observed, in these cells which show large hysteresis, the relative size of the crystals used. Were they fine or coarse?

DR. WOLFF: They were both. Larger hysteresis is, of course, to be expected with the white samples of mercurous sulphate, most of which were coarse grained.

PROF. CARHART: My experience would lead me to think that the hysteresis was dependent largely, at all events, on the size of the crystals of the cadmium sulphate, but there are certain differences due to fusion. If the crystals are ground up and put in the cell, after the cell has stood for some time, the crystals will form a solid mass. They become apparently solidified in the cell, and are almost equivalent to one big crystal, so that a change of temperature under these circumstances would not be followed rapidly at all, not in forty-eight hours, by a corresponding change in the concentration of the solution. The solution would change with a rise in temperature, and be over saturated on a falling temperature. It is a great question as to how large the crystals of cadmium sulphate ought to be. If the cells are kept in a bath, at a constant temperature, continuously, it makes no

difference what the size of the crystals is. With the varying temperature it does make a difference on account of the solubility and the recrystallization. I might add that my experience in making Weston normal cells, as I prefer to call them, which extends over several years, leads me to think that the cell made with precipitated mercurous sulphate, chemically precipitated, is a better cell than cells made with the electrolytic mercurous sulphate. I would not wish to state that conclusion as final, but experiments running over some time indicate that in my own case. I get more uniform results with the precipitated murcurous sulphate than I do with the electrolytically prepared murcurous sulphate.

Mr. Carl Hering: Where was the thermometer placed to show the hysteresis? Might it not be a temperature phenomenon that is lagging of the equalization of temperature, instead of being electrolytic? I understand that these very small differences of voltages are measured by comparison with some standard cell which remains unchanged, and that there is no method of directly measuring voltages as accurately as that, except by comparison with some standard cell which is supposed to remain standard.

Dr. Wolff: We made our measurements against a set of eleven cells, which remained in another thermostat constantly at twenty-five degrees. As to the measurement of temperature of the cells, they were totally immersed to a depth of two or three centimeters in an oil bath which was thoroughly stirred. Tests with a platinum thermometer showed that differences in temperature in different parts of the bath were less than one hundredth of a degree centigrade.

In regard to Professor Carhart's remarks, there are three questions which were brought up, first as to whether these results will affect the value of the cell as a fundamental standard. Of course all present will understand that the cell can be kept at a constant temperature indefinitely. The question of hysteresis only enters when the cells are subjected to relatively rapid temperature changes and when we assume that a freshly made up cell will immediately take its normal value. A number of our cells which showed considerable hysteresis were among those which had high initial values which persisted for some weeks. I think, therefore, that the existence of hysteresis will help us

find defects in the specifications we have heretofore overlooked. This we have not yet had time to investigate.

Second, in regard to the size of the grain, no effects similar to those found with finely ground mercurous sulphate have been observed in the case of cadmium sulphate. We included in our measurements some cells obtained from Professors Carhart, Hulett, Guthe and others, with large cadmium sulphate crystals, and some of our own, set up in the same way with a much larger number of finely crushed crystals. No differences in respect to hysteresis were found. Without any question the trouble lies in the paste limb.

Third, in regard to the difference between the electrolytic and the chemically prepared mercurous sulphate; at the Bureau we prepared cells from samples made by seven or eight different methods, and we found no consistent differences between them; in fact, we find a better agreement among the cells set up with the electrolytically prepared samples of mercurous sulphate than the others. Among the cells which exhibit discrepancies are quite a number set up with coarse grained white samples of mercurous sulphate. I rather think that from the standpoint of hysteresis the size of the grain of mercurous sulphate is only important when the grains are quite large and therefore expose a relatively small surface, thus retarding the establishment of concentration equilibrium.

Mr. F. A. Lidbury: I would ask one question in regard to the periods of time during which these cells were kept at one certain temperature, were measurements taken during these periods of time, and did they show, towards the ends of these periods, an approach to a steady value?

Dr. Wolff: They were measured every twenty-four hours, and in some cases the cells were kept at the same temperature five or six days. The abnormal cells approached the normal value, as might be expected.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., April 30, 1908; President C. F. Burgess in the Chair.

THE PRINCIPLES INVOLVED IN THE SELECTION AND DEFINITION OF THE FUNDAMENTAL UNITS TO BE PROPOSED FOR INTERNATIONAL ADOPTION.

By F. A. Wolff.

INTRODUCTION.

In a paper presented to the International Electrical Congress at St. Louis, in 1904,[1] the writer reviewed the efforts which had previously been made to secure international uniformity of the electrical units, and pointed out their failure as shown by the discrepancies in the laws thus far enacted.

These efforts practically begin with the Siemens' unit and the C. G. S. system of the British Association, of which the practical unit of resistance, intended to represent 10^9 electromagnetic units, took a concrete form.

As pointed out in the paper referred to, the error found in the B. A. unit led to the convocation of the first International Electrical Congress, in 1881, which recommended that the practical electrical units be defined in terms of the C. G. S. (electromagnetic) units, and that the unit of resistance be represented by a column of mercury 1 sq. mm. in cross-section, at the temperature of 0° C. and of a length to be determined by an international commission on the basis of new absolute measurements.

In accordance with the above, the International Commission which met in Paris, in 1882 and 1884, recommended the following definitions:

The legal ohm is the resistance of a column of mercury 1 square millimeter in cross-section and 106 centimeters in length at the temperature of melting ice.

The ampere is equal to one-tenth of a C. G. S. unit of the electro-magnetic system.

[1] Transactions St. Louis Int. Elec. Cong., 1, 148 (1904). Bulletin Bureau of Standards, 1, 39 (1904).

The volt is the electromotive force which will maintain a current of one ampere in a conductor of which the resistance is a legal ohm.

It will thus be seen that a distinction was made between the concrete and the absolute ohm. The ampere was defined in terms of absolute units, while the unit of electromotive force was derived from a concrete unit of resistance and an absolute unit of current.

The last formal international action was taken by the Chicago Congress of 1893, which adopted the following definitions:

"*Resolved,* That the several governments represented by the delegates of this International Congress of Electricians be, and they are hereby, recommended to formally adopt as legal units of electrical measure the following:

As a unit of resistance, the *international ohm,* which is based upon the ohm equal to 10^9 units of resistance of the C. G. S. system of electro-magnetic units, and is represented by the resistance offered to an unvarying electric current by a column of mercury at the temperature of melting ice, 14.4521 grammes in mass, of a constant cross-sectional area and of the length of 106.3 centimeters.

As a unit of current, the *international ampere,* which is one-tenth of the unit of current of the C. G. S. system of electro-magnetic units, and which is represented sufficiently well for practical use by the unvarying current which, when passed through a solution of nitrate of silver, and in accordance with the acompanying specifications, deposits silver at the rate of 0.001118 of a gramme per second.

As a unit of electromotive force, the *international volt,* which is the electromotive force that, steadily applied to a conductor whose resistance is 1 international ohm, will produce a current of 1 international ampere, and which is represented sufficiently well for practical use by 1000-1434 of the electromotive force between the poles or electrodes of the voltaic cell known as the Clark's cell, at a temperature of 15° C., and prepared in the manner described in the accompanying specifications."

The disagreement of the laws defining the units subsequently enacted by the various countries may be traced to the following causes:

First.—The three fundamental units, although connected by Ohm's law, were either directly or indirectly defined in terms of concrete standards, naturally resulting in inconsistencies in the definitions, which by new measurements of the value of the Clark cell were shown to be almost one-tenth per cent.

Second.—The specifications were not sufficiently definite, thus limiting the accuracy of reproduction.

Third.—In the definitions adopted, the *international* units were not recognized as separate and distinct from the *absolute* units on which they were based.

As some of the laws were enacted before and some after the inconsistencies in the definitions were recognized, considerable differences resulted, a subject fully discussed in the paper above referred to. For our present purpose it need only be recalled that in some cases the same unit was defined effectively in as many as three or four different ways in the same law. Official international recognition of the discrepancies between the laws was taken by the St. Louis Congress, which adopted resolutions to the effect that the questions could best be dealt with by an international commission representing the governments concerned, that such a commission might in the first instance be appointed by those countries in which legislation on electric units had been adopted, and that provision should be made for securing the adhesion of other countries prepared to adopt the conclusions of the commission. The hope was expressed that the commission referred to might eventually become a permanent one.

In accordance with the provisions of the above resolution, invitations were extended to England, France, Austria, Belgium and the United States, by Professor Warburg, president of the Reichsanstalt, on behalf of Germany, for a conference which was held in Berlin, in October, 1905. The decisions reached by the Berlin conference[2] were as follows:

First.—That only two electrical units shall be chosen as fundamental units.

Second.—The international ohm, defined by the resistance of a column of mercury, and the international ampere, defined by the deposition of silver are to be taken as the fundamental electrical units.

Third.—The international volt is the electromotive force which produces an electric current of one international ampere in a conductor whose resistance is one international ohm.

Recommendations were also made that more detailed specifica-

[2] Verh. Int. Konf. Elektr. Masseinheiten, p. 42.

tions be adopted for the mercury ohm, and that the Weston cadmium cell with solid hydrated cadmium sulphate and a 12 to 13 per cent. cadmium amalgam be adopted as the standard cell.

The opinions were further expressed by the conference:

"First.—That the information before it is not sufficient to enable it to propose any alteration in the formerly accepted value for the ampere.

"Second.—That the information before it is not sufficient to enable it to lay down exact directions in respect to the silver voltameter and the standard cell.

"Third.—That if a proposal for a change in the accepted value of the ampere is to be brought from any source before a formal conference to be held later, an agreement in writing on the point should be come to previously between the parties interested. If differences of opinion in the matter cannot be removed, a new preliminary conference should be held. The same procedure should be observed in regard to the specifications for the silver voltameter and the standard cell, in the event of such specifications being submitted to a formal conference from any quarter."

The recommendations made at the conference by Professor Carhart and by the Bureau of Standards, that the volt be selected as the second fundamental unit were rejected, as were also the recommendations of the Bureau advocating a systematic program of absolute measurements before the next international electrical congress was called.

The conclusions reached by the Berlin conference should be regarded as preliminary in view of the fact that considerable work has since been done on both the standard cell and coulometer, particularly as the conference expressed the opinion[3] that the information before it was not then sufficient to enable it to lay down exact directions with respect to the silver voltameter and the standard cell.

The questions likely to be considered by the next International Congress, for which it is proposed to issue a call in the near future, are as follows:

First.—The selection of the two units to be taken as fundamental, and in terms of which all the others will be derived.

Second.—The adoption of specifications for the units selected.

[3] Verh. Int. Konf. Elek. Masseinh., p. 50.

Third.—The adoption of numerical values in the definitions of the fundamental units.

Fourth.—The definition of the remaining international electrical units in terms of the two taken as fundamental.

Fifth.—The definition and naming of the international magnetic units.

Sixth.—The discussion of international photometric standards. Of these, the last two topics will not be discussed in this paper.

THE CHOICE OF THE FUNDAMENTAL UNITS.

As it is universally agreed that the ohm be taken as one of the two fundamental units, the question is reduced to the choice between the ampere and the volt, defined respectively in terms of the coulometer and standard cell, as the second unit.

In the opinion of the writer[4] it would be well, before a final decision is made, to consider fully the principles involved in the choice, which should, of course, be made on the basis of merit and without prejudice or undue deference to previous practice.

Arranged in the order of their importance, these are:

First.—Accuracy of reproduction from specifications.

Second.—Concreteness.

Third.—Ease of reproduction.

(1) Accuracy of Reproduction.

The factors determining the accuracy of reproduction in the case of the coulometer and the standard cell may be stated to be:

(a) The nature of the fundamental principle underlying the definition;

(b) The purity of the materials employed;

(c) The number of measurements involved in the realization of the definition.

(a) The preference heretofore generally given to the coulometer can be attributed in part to the fact that its indications are assumed to be exact, being based on Faraday's law, generally regarded as a fundamental law of nature. The more recent work[5]

[4] Bulletin Bureau of Standards, **1**, 50-59 (1904).

[5] Richards, Collins and Heimrod, Proc. Amer. Acad., **35**, 123 (1900); **37**, 415 (1902). Zeitsch. Phy. Chem., **32**, 321 (1900), and **41**, 302 (1902); Guthe, Phys. Rev., **19**, 138 (1904), and Bull. Bur. Stand., **1**, 21 and 349 (1904-1905). Carhart, Willard and Henderson, Trans. Amer. Electrochem. Soc., **9**, 375 (1906). Van Dijk, Ann. Phys., **19**, 249 (1906).

on the coulometer seems, however, to establish the conclusion that while Faraday's law may be rigorously exact, account must certainly be taken of the possible effect of secondary reactions accompanying the electrolysis, thus complicating the results as shown by the differences obtainable in the use of coulometers of different types. On the other hand Smith[6] obtained "Identical values within one or two parts in 100,000 for the electrochemical equivalent of silver for six different types" and "no influence of pressure, temperature or current density." Dushak and Hulett[7] have, however, recently found for the porous cup type a difference of almost .01 per cent. between the deposits formed in the presence and absence of air. The difference was further established by an analysis of the deposited silver, which on heating gave up water and gas. Dushak and Hulett state that "the idea of the included matter being other than trapped electrolyte finds support, first in the constancy of the quantity of impurity in deposits formed under the same conditions, and second, in its apparent uniform distribution throughout the silver crystals." The writer, while disclaiming any intention of discrediting the work of any of the investigators, simply desires to call especial attention to the discrepancies in their results, which indicate that either the same procedure has not been followed by all, or that unrecognized sources of variation exist. It cannot, therefore be regarded as established that the *increase of weight* in the coulometer is in strict acordance with Faraday's law.

The principle underlying the definition of the volt is equally fundamental, though not capable of expression in as simple a form as Faraday's law, since electrode potentials are determined solely by the nature, concentration and temperature of the materials involved. In reversible cells these are not changed by the passage of small currents in either direction.

The formula which expresses the relation and which was first deduced by Helmholtz from thermodynamical principles, may be put in the form

$$Q = Ct\left(ET\frac{dE}{dT}\right)$$

in which Q represents the *total* energy of the reaction, including that set free or absorbed in solution, hydration, change of state,

[6] Phil. Trans. Roy. Soc., **207**, 581 (1908).
[7] Dushak and Hulett, Trans. Amer. Electrochem. Soc., **12**, 257 (1908).

etc.; E, the electromotive force; T, the absolute temperature, and Ct the number of coulombs corresponding to the reaction. It follows, therefore, that if, for the particular reaction, there is a constant relation between the number of coulombs and the total energy per gram molecule, as well as a constant relation between the free and total energy, the electromotive force must have a definite value for given external conditions.

Since the first condition does not involve any assumption as to the simplicity or complexity of the ions, or even as to the nature of electrolysis, and since the second must be granted as being based on the fundamental principles of thermodynamics, it will be seen that the electromotive force of a reversible voltaic combination follows a law quite as rigorous as that of Faraday. In case of the silver coulometer, secondary products, the electrolysis of which would modify the result, may be formed, but in the case of the standard cell no secondary reactions of this kind need be considered as the electromotive force of the cell is always compensated, so that there is only a negligible amount of electrolysis produced. Reactions may, however, take place between the ingredients in the cell which give rise to secondary products affecting the electromotive force, but as both Clark and Weston cells can be constructed which will maintain their values for considerable periods, such reactions are either absent, or take place very slowly, so that they need not be considered in discussing the accuracy of reproduction. The question of constancy will be taken up under the next heading.

(b) The question of the purity of the materials employed is most important in both cases, with the advantage resting slightly with the silver coulometer, as the number of materials is less. On the one side it is necessary to start with pure silver and silver nitrate, while on the other hand pure cadmium and cadmium sulphate (or zinc and zinc sulphate), together with mercury and mercurous sulphate, are required. It will be generally admitted that the metals silver, cadmium, zinc and mercury can readily be prepared in the highest state of purity, as also the silver nitrate and zinc and cadmium sulphate. The recent work on the standard cell has demonstrated that mercurous sulphate of uniform electromotive properties can also be obtained by a number of different methods, so that it might be considered that there is

little choice on the basis of the number of materials entering into the coulometer and cell. The question of the purity can, however, almost be eliminated if arrangements be made by the national standardizing laboratories to furnish the necessary materials, which can be prepared in considerable quantities by the best methods, so that this would not have to be done by each investigator.

(c) The greater number of materials required in the cell is more than offset, on the other hand, by the number of measurements, each subject to possible error, which must be made in the case of the coulometer to realize the ampere from its definition. The cell automatically takes a value determined by the materials employed, while the results of a coulometer measurement depend on two washings and subsequent weighings made with the greatest quantitative care (particularly the last on account of the granular and loosely adherent character of the deposited silver), the regulation of the current during the run, as well as an accurate measurement of its duration.

The author wishes to lay particular stress on the fact that while standard cells set up by different individuals in different laboratories have been compared in order to establish the accuracy of reproduction, the corresponding step has not as yet been taken with reference to coulometer measurements, so that the results obtained by different investigators only establish relative reproducibility. The indirect comparison is now possible owing to the progress made in the construction of standard cells and standard resistances which may be carried from place to place, and through which alone the results of coulometer measurements made in different localities can be accurately compared. Before making a final choice, the relative merits of the cell and coulometer with respect to accuracy of reproduction should, however, be definitely established by a systematic campaign of international co-operation involving the exchange of specifications and materials by the various national laboratories, each of which would undertake to make a careful series of coulometer measurements and to set up a considerable number of cells in accordance with the various specifications proposed. The value of the results obtainable can be further increased by the co-operation of the national bureaus with qualified individuals in the respective coun-

tries. All the results could subsequently be reduced to a common basis of comparison, through the interchange of resistance standards and standard cells.

(2) Concreteness.

Another most important consideration is that the definitions of the units adopted as fundamental should both be capable of realization in the form of concrete standards. This makes possible the construction of standards which will maintain their values for considerable periods at least, and in terms of which measurements can, at all times, be made. It also makes possible the direct intercomparison of the concrete standards of the various laboratories by the exchange of standards designed for portability.

In this respect the standard cell has, perhaps, its greatest advantage over the silver coulometer, which merely gives the average value of a current which has been passed through it, and which has ceased to exist. The result of the measurement is, therfore, a silver deposit, and not a standard in terms of which other current measurements can be made, making it necessary to employ a standard resistance and a standard cell as secondary units to fix the results. Both the secondaries must be assumed to remain constant between coulometer measurements which are ordinarily made at long intervals. The more recent work has shown that both Clark and Weston cells can be set up which will maintain their values, within one part in 100,000, for considerable periods, and that when properly set up they will assume their normal values immediately. It is true, however, that some Weston cells have been under observation which have decreased in voltage with time. Hulett attributes this to an unstable equilibrium in the paste limb, but this cannot be regarded as established, as the effect may possibly be due to imperfect washing of the mercurous sulphate prepared in strongly acid solutions, or to traces of impurities in the materials employed. A number of cells with abnormal values have been under observation at the Bureau for some time, and were included with others in a redetermination of the temperature coefficient, in the course of which it was found that they exhibited enormous hysteresis. As the mercurous sulphate was originally present in considerable excess

it seems that the retardation of the establishment of concentration equilibrium may be due to the formation of a difficultly soluble surface film. It is hoped than an analysis of the materials, which will shortly be undertaken, will definitely establish the cause of the abnormal behavior. Even though the Weston cell should be found to represent a system in unstable equilibrium, and should be rejected, the Clark cell, in which no abnormal behavior has thus far been observed, would still be available as the concrete standard of electromotive force. The cracking at the amalgam limb can be overcome by suitable construction, and the objections on account of the high temperature coefficient can be practically eliminated by the employment of thermostats. With the attributes of *constancy* as well as *reproducibility* established, the standard cell would have greater merit than the mercury ohm, since the mean value of a number of fillings is always taken in order to eliminate errors of filling, and since in the interval between mercury ohm measurements, the results are usually carried by manganin copies and not by the primary standards.

(3) Ease of Reproduction.

In respect to ease of reproduction the standard cell again has the advantage. In the first place the facilities required for a coulometer measurement, consisting of a precision balance, calibrated weights, platinum bowls, accurate time service and means for accurately measuring the duration of a run, together with a supply of purified silver and silver nitrate, are to be compared with the necessary cell blanks, and a supply of specially prepared or purified cell materials. For results of the highest precision the balance must, in addition, be especially protected from temperature changes, and provision must be made for controlling the humidity in the balance case.

In the case of the coulometer the operations consist in washing, drying and weighing the cathode dish before and after receiving its deposit, in maintaining the current at a constant value during the run and in the measurement of the duration of the run, all of which operations and measurements must be performed with the highest quantitative care, while the operations involved in setting up a standard cell require only care in washing the mercurous

sulphate since relatively large variations in the composition of the amalgam only slightly affect the electromotive force.

Although the time required for setting up a few cells might be greater than that required for a corresponding number of coulometer measurements, if the time for purifying the materials were included, it must be remembered the latter could be prepared in considerable quantity and preserved under proper conditions for future use. This could also be undertaken by the national laboratories, from which investigators could obtain them from time to time. The main conclusion under this head is, therefore, that while in the case of the coulometer, special facilities are required and numerous *quantitative* measurements and manipulations must be made in order to make a single current measurement, the manipulations required in setting up a standard cell are all *qualitative* and less in number, so that, without special facilities and in the hands of individuals of equal skill a higher accuracy of reproduction should be obtained.

The question of ease of reproduction, while not of the highest importance, should nevertheless be considered from the standpoint of all who deal with electrical measurements of precision and who should not be compelled to depend any more than necessary on the national laboratory. It has, however, been held that facility of reproduction is no great advantage, since similar experimental difficulties result from the definition of the ohm in terms of the mercury column. With the ampere taken as the second fundamental unit, the construction of mercury ohms and coulometer measurements would infrequently be undertaken, mainly by the national laboratories. In this case it is necessary to resort to wire copies of the mercury ohm on the one hand, and standard cells on the other, each regarded as secondary.[8]

The case appears to be, however, very different, as in the definition of unit resistance in terms of the mercury column we are left without any satisfactory alternative, so that we are forced to resort to secondary standards, multiples and sub-multiples of which can readily be constructed and compared. On the other hand we might select either the coulometer or the standard cell as the second fundamental unit. In the first case the result can only be fixed by the aid of some current measuring device, the

[8] Mitth. Reichsanstalt, E. T. Z., 25, 671 (1904).

best of which have a limited accuracy, or, as is usually done, by the combination of a standard resistance and a standard cell, the latter being taken as the secondary standard. In the second case the cell is taken directly as a fundamental standard. It will, therefore, be seen that the standard cell, which itself, satisfies the requirements of a fundamental standard as well as the mercury ohm, should not be regarded in the same light as wire copies of the latter which cannot be reproduced from specifications.

The question of choice should also be regarded from the standpoint of the national standardizing institution. As the selection of the ohm and ampere necessitates the adoption of the standard cell as a secondary unit to fix results in the interval between coulometer measurements, the value to be taken for the cell will involve the errors introduced in the reproduction of the mercury ohm as well as those involved in the coulometer measurements, so that unless these together are less than the differences met with from time to time in setting up standard cells directly from the specifications or from materials drawn from the same source, the question would certainly arise as to whether the value to be adopted for the cell should be changed to correspond with each reference to the mercury ohm and coulometer, or whether weight should be given to previous results in the face of a possibly more accurate agreement between old cells and cells freshly set up. In this connection attention should be called to the practice in Germany where the ohm and ampere are taken as fundamental units. In 1896 and 1898 two series of coulometer measurements were made to determine the values of the Clark and Weston standard cells. The results,[9] which differed by over .02 per cent. from the directly determined ratio, were adjusted and the values of the Clark and Weston cells thus derived have been in use ever since in Germany. In effect the standard cell has been employed as a fundamental standard, since, by ignoring the definition of the ampere, the result obtained is equivalent to legalizing the values found for the standard cells.

Further light is thrown on this phase of the question by the practice at the Reichsanstalt in reference to the unit of resistance; four manganin standards have been referred, from time to time, to the mercury units of that institution,[10] but since 1898 the mean

[9] Kahle., Zeitsch. Instkn., **18**, 229 and 267 (1898); Wied. Ann., **67**, 1 (1899).
[10] Ber. Int. Konf., 1905, p. 63; Zeitschr. Instkn., **26**, 15 (1906).

value of the four coils has been assumed constant, as the apparent changes of the mean were found to be within the limits of accuracy with which the mercury ohms could be produced. It is therefore confidently predicted that the standard cell, which must be depended on between coulometer measurements, will, even if the ohm and ampere are taken as fundamental units, in effect replace the coulometer, unless the accuracy attainable through the ohm and ampere is found to exceed the accuracy with which the cell can be reproduced.

This is a point of considerable importance from the standpoint of the standardizing institution, on account of the fact that standard cells and not coulometers are submitted for certification, making it necessary to adopt values for the reference cells in terms of which results are expressed.

Moreover, since in actual practice, instantaneous values of currents and voltages of any magnitude are measured with the greatest ease and accuracy directly in terms of resistance standards and standard cells, the choice of the ohm and volt as fundamental units is the more logical.

SPECIFICATIONS.

In reference to the adoption of specifications for the units chosen, attention has already been called to the opinion expressed at the Charlottenburg conference to the effect that the information before it was not regarded as sufficient to enable it to lay down exact directions with respect to either the silver voltameter or the standard cell. Considerable work has since been done along both lines, but no systematic comparison has been made of the specifications proposed by the various investigators. As the principal object of the next congress will be to redefine the international units in terms of concrete standards reproducible to the highest attainable accuracy from specifications, the latter must be drawn with the greatest care. The various specifications proposed, which differ in regard to details, should therefore be carefully subjected to comparison by numerous investigators, so that any unrecognized defects might be brought to light. It is felt that this would be one of the important objects of the international co-operation above proposed, since by the aid of the national laboratories, all results could be reduced to the same basis of com-

parison and differences which might be found and which might furnish a clue to defects in the specifications could be further investigated.

Values to be Adopted for the Units.

In the first place it is necessary to recognize that the C. G. S. system, while giving us *ideally* perfect definitions of the electrical units, fails in practice owing to the necessarily limited accuracy of the absolute measurements in comparison with the precision attainable in relative measurements. The desirability of referring results to concrete standards, was recognized by the British Association in the proposal of the B. A. unit of resistance, intended, and for some time supposed to represent 10^9 C. G. S. electromagnetic units. With the advances made in the construction of the mercurial resistance standard, the first Paris congress recommended its adoption for defining the unit of resistance, notwithstanding the great improvements made up to that time in absolute measurements, the choice being made on the basis of accuracy of reproduction of the results. This was also the principle guiding the Chicago congress in substituting for the mean cross-section of the mercury column, the mass of mercury corresponding to a stated length, following the already established practice of employing the liter instead of the cubic decimeter for volumetric work. As all resistance measurements are now referred to the mercurial unit without reference to its relation to the absolute ohm, this should also be done with the second fundamental unit. In other words the absolute and international units should be recognized as separate and distinct, so that in the definition of the latter no reference need be made to the former. The particular values adopted in the definitions of the international units should, however, be selected to secure approximate agreement with the absolute units which they will replace for all practical as well as scientific purposes. The few measurements which it is occasionally necessary to also express in absolute units could be reduced to the same by applying a correction factor obtained from the results of the various absolute measurements, all in turn fixed by being expressed in terms of the reproducible concrete standards employed to define the international units.

As the values adopted by the next conference should be

allowed to stand for at least 25 years, to limit the confusion naturally involved in any change of the basis of reference, it seems desirable before making a decision as to the numerical values to await the results of further absolute measurements, a number of which are already under way, since with the great advances made within the last ten years in absolute measurements it might confidently be expected to keep the errors within .01 per cent., thus making the difference between the absolute and international units practically negligible. With this degree of approximation the numerical values employed in the definitions could be allowed to stand indefinitely until some better method of defining the units is recognized.

The writer expressed himself on this subject at the St. Louis congress and found opposition to the plan, particularly on the part of some of the foreign representatives, who strongly advocated adherence to the absolute units, though recognizing the necessity of concrete standards the values of which it was proposed to alter from time to time to bring them into better accord with the latest absolute measurements. The objection of confusion as to the basis of reference in the literature, has already been pointed out above. In addition, unless the question were regulated by an international commission, each national laboratory would be inclined to give greater weight to its own absolute measurements, thus defeating the aim of international uniformity. The better way would be to consider the international units as fixed for a definite period, and the relation between these and the corresponding absolute units could be reported on from time to time by an international commission in the light of all the data before it.

This should dispose of the argument in favor of the coulometer to which considerable weight seems to have been attached, that a current can be directly measured in terms of the absolute units, whereas the unit of electromotive force must be derived from the absolute measurement of resistance and current. The definition of the ampere in terms of some specific value taken as the electro-chemical equivalent of silver would, with the unit of resistance fixed, result in fixing the value of the standard cell within the limits of error involved. The numerical value for the cell would, however, be exactly the same if derived from the same

absolute current and resistance measurements on which the definitions of the international ohm and ampere are based.

It has also been claimed that the choice of the volt as a second fundamental unit would result in the ohm entering twice into the derivation of unit current. It is, however, evident that this is not the case so long as the unit of resistance, from which the value of the cell is initially determined, remains constant. This makes the question raised an academic one, since in practice all current measurements are directly referred to a standard cell and a standard resistance.

DERIVED UNITS.

It will be generally agreed that the remaining units, capacity, inductance, magnetic flux, power, energy, etc., should all be defined in terms of the definitions adopted for the fundamental units, notwithstanding that they are now defined in terms of the C. G. S. system, as a distinction can be made by designating the units thus defined as international. If the values adopted for the international units agree with the absolute units, upon which they are based, to within even one part in 2,000, as will certainly be the case, no serious objections can be made as the replacement of the absolute units will be fully justified by the greater accuracy of reproduction made possible.

SUMMARY OF CONCLUSIONS.

First.—The decisions of the Berlin conference of 1905 should not be regarded as binding, in view of the large amount of work since published on the silver coulometer and standard cell.

Second.—The international electrical units to be adopted should be regarded as separate and distinct from the absolute units on which they were originally based.

Third.—The choice between the ampere and the volt should be made exclusively on the basis of merit.

Fourth.—That the principles on which the decision should be made are:

a. Accuracy of reproduction from specifications.
b. Concreteness.
c. Ease of reproduction.

Fifth.—The accuracy of reproduction of the coulometer remains to be established, as coulometer measurements made by different investigators establish only relative accuracy, no accurate comparisons of the results obtained by different investigators having thus far been made.

Sixth.—If a decision must be made at the present time and on the basis of merit, the cell should be selected on account of the advantages it offers from the standpoint of concreteness and ease of reproduction, since no greater accuracy of reproduction can be claimed for the coulometer in the light of the data at hand. In addition, this choice is more logical from the standpoint of the standardizing laboratory as it leads to fundamental units corresponding to the standards submitted for certification as well as corresponding to the practice of measuring currents in terms of standards of resistance and electromotive force.

Seventh.—In view of the preference indicated for the coulometer at the Berlin conference, the reproducibility of the cell and coulometer should, however, first be definitely established by systematic international co-operation, which would also result in bringing to light unrecognized defects in the specifications proposed.

Eighth.—If the ampere is defined in terms of the coulometer the value to be taken for the standard cell, which must be depended on between coulometer measurements, must be determined at each of the national standardizing institutions, the results obtained reduced to a common basis by exchange of cells and resistance standards, and a mean value taken to insure international uniformity.

Unless the accuracy of the result, involving errors in the realization of both the ohm and ampere is greater than that attainable in the reproduction of the cell from specifications, the definition of the ampere will subsequently be ignored, making the cell in effect a primary standard. The same result can be more directly obtained by selecting the volt as the second fundamental unit since a practically equivalent value may be assigned to the cell, in which case the corresponding value for the electro-chemical equivalent of silver need not be known to the highest accuracy, as it could only be used for the purpose of loosely defining the ampere.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., April 30, 1908; President C. F. Burgess in the Chair.

THE CONSTRUCTION AND ACCURATE MEASUREMENT OF RESISTANCES OF THE ORDER OF ONE HUNDRED THOUSAND MEGOHMS.

By Howard L. Bronson.

The study of the passage of electricity through gases and its application to the measurement of the phenomena of radioactivity has required us to extend our field of accurate electrical measurements. During the past ten years, we have become very familiar with the fact that X-rays, ultra-violet light and many substances, such as uranium, radium and thorium *ionize* the gas in their immediate vicinity—that is, the gas becomes electrically conducting. If the gas between two parallel plates is subjected to a constant source of ionization, and one plate is connected to the positive pole of a battery, the other pole of which is to earth, and the other plate is connected to an electrometer, then the electrometer will receive a positive charge, showing that an electric current is passing between the two plates. The magnitude of these ionization currents, which we measure, varies from 10^{-15} amps. up to currents which can be measured with a sensitive galvanometer. The accurate measurement of the smallest of these currents is by no means an easy task, but the problem is much complicated by the fact that in a large part of radio-active measurements the active matter, and, therefore, the current, is not constant, but continually changes, and sometimes very rapidly. For example, the emanation from thorium decays to half-value in a little less than one minute. Thus, if we have in a testing vessel a current of 10^{-8} amps. due entirely to thorium emanation and suddenly cut off the supply of the emanation, the current will fall to $\frac{1}{2000}$ of its value in ten minutes.

The problem, as presented, is to get an instantaneous measure-

ment of very small currents. The apparatus must, at the same time, be capable of a considerable range of measurement without serious readjustment. The purpose of this paper is to describe a method which theoretically fulfills these requirements, and which, for many kinds of radio-active measurements, the writer has found to give better results practically than the methods in more common use. It will be seen that this method depends entirely on our ability to make and measure resistances which are sufficiently large and at the same time constant.

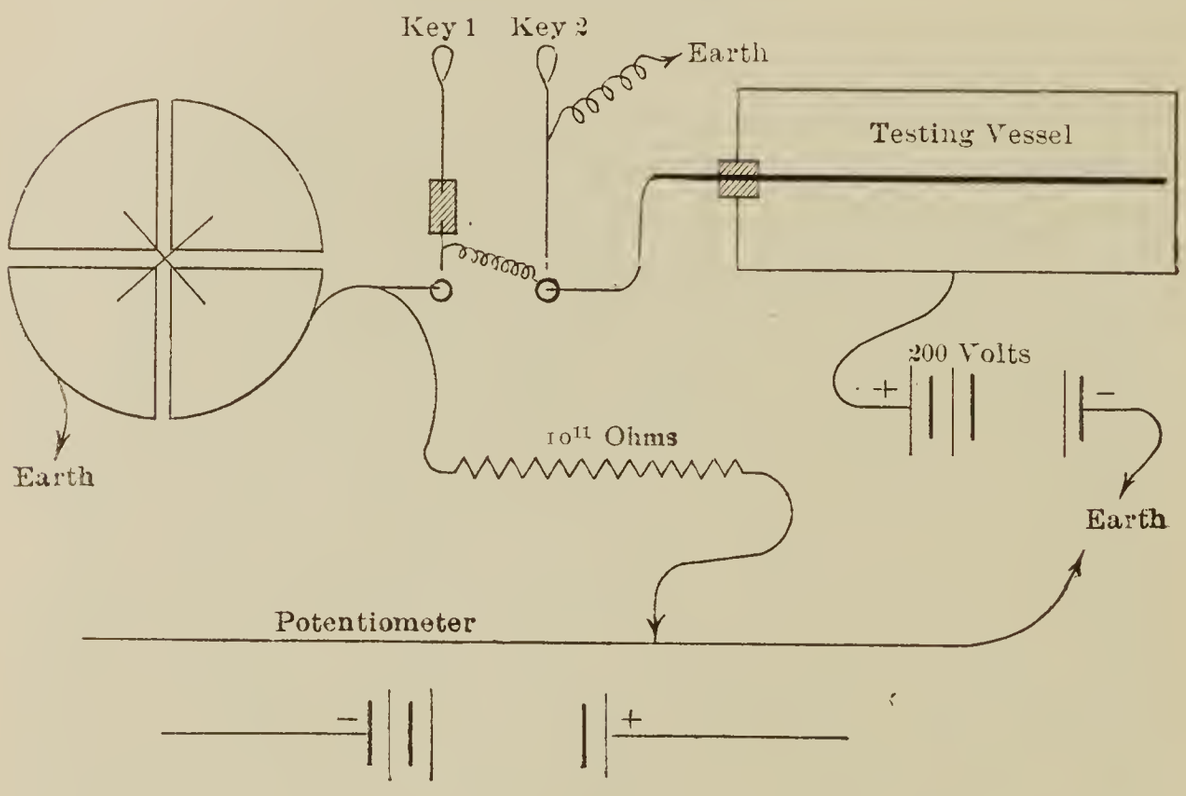

Fig. 1.

As far as the writer is aware, all the older methods for the measurement of these very small currents involve the direct measurement of the change of potential of some system of known capacity. The electroscope is probably the most sensitive instrument for this purpose, as it can be made with a capacity as small as one electrostatic unit, and a change of potential of 5 volts per hour can be measured. The electrometer, while not quite so sensitive, can measure currents over a much wider range, by the introduction of external capacity into the system A subdivided condenser is very convenient for this purpose.

The use of either of these instruments for the accurate

measurement of currents involves many difficulties. The chief difficulty in their use for certain radio-active measurements is that a single observation requires considerable time, during which the current may have changed very greatly. Among the other difficulties may be mentioned:

(1) Changes in the sensitiveness of the instruments.

(2) Lag of the electrometer needle or gold leaf behind the changing potential, unless its rate of change is very slow.

(3) The accurate measurement of small capacities, which have to be redetermined every time a new testing vessel is used.

(4) The long time necessary for the measurement of the natural leak.

In fact, we can say that this method is practically impossible for rapidly changing currents and that it is in all cases inconveniently slow.

The principle of the "constant deflection method," which is described below, is very simple and was first suggested by Rutherford. If one pair of quadrants of an electrometer is connected to earth, Fig. 1, and the other pair is not only connected to the testing vessel, but also to earth, through a very high resistance, it is easily seen that any current in the testing vessel will charge the quadrants, until the discharge current through the high resistance is equal to the current in the testing vessel. (This latter current is not diminished by the rise of potential of the quadrants, because the voltage on the testing vessel is always high enough to produce practical saturation.) In this case, the current is proportional to the potential on the quadrants—that is, to the deflection of the needle. If the sensitiveness of the electrometer and the actual value of the high resistances are known, then we have at once an absolute measure of the ionization current in the testing vessel. Further, by placing some form of potentiometer between the standard high resistance and the earth, the range, over which we can measure currents, can be made very large.

The advantages of this method are obvious; deflections are independent of the capacity, and testing vessels may, therefore, be interchanged without error, measurements can be made over a wide range without difficulty, and observations can be taken instantaneously and in as rapid succession as desirable.

This method has also several *practical* advantages. In the rate methods, if the current due to the *natural ionization* and the conduction across the insulators is small, then it takes a long time to measure it; if it is large, then it may become a considerable fraction of the current to be measured, and reduces the accuracy of the measurement. In the constant deflection method, small currents are as quickly measured as large ones, and a considerable amount of insulation leakage introduces no considerable error in the results. When desirable, this can be practically eliminated by keeping the electrometer quadrants at zero by means of a potentiomenter. By referring to Fig. 1, it will be seen that there are two keys between the testing vessel and the electrometer. When both keys are closed, the testing vessel and the electrometer quadrants are connected to earth; when key 2 is open, the earth connection is broken and the testing vessel is connected to the electrometer; when key 1 is open, the electrometer is disconnected from the testing vessel, but remains connected to earth through the high resistance standard. The reading obtained in this way is the true zero, and eliminates certain contact potential differences which have always been found to exist in all very high resistance standards. This zero can be checked at any time during the course of an experiment. Before any active material is placed in the testing vessel, the natural leak is obtained by taking a reading with key 2 open and subtracting from this the true zero. This reading is just as quickly taken as any other, and it is evident that its magnitude practically does not affect the accuracy of the measurement to be made with this vessel. It can thus be seen that the method is simpler, more accurate and better suited for nearly all kinds of ionization measurements than the older methods.

The problem then resolves itself into finding out how to make and preserve permanent high resistances of the order of 10^{11} ohms. The great difficulty in doing this is probably the reason that this method has not come into more general use. The writer is still far from satisfied with his own attempts, and would be very glad to receive any suggestions. Very early in the study of this subject it was found possible to get resistances as large as 10^{11} ohms by means of fine carbon lines on ebonite or ground glass, or by means of amyl alcohol or xylol in long

capillary tubes. Measurements of ionization currents with these resistances as standards compared favorably with those obtained by the *rate* methods. There was always, however, considerable variation and uncertainty in all these resistances. The carbon line seemed to have practically its entire resistance at one point and to be merely a case of bad contact, which was bound to be very uncertain and subject to all kinds of external conditions. The liquid resistances have very large temperature coefficients, and seemed to be subject to a variable polarization. In both classes of resistances, there was necessarily present a considerable amount of insulating or dielectric material. The absorption due to this is a function both of the time and temperature. Its effect is to make the apparent resistance less for a time. It may continue for some hours, and is necessarily a very uncertain factor.

All these high resistances proved so unsatisfactory that Professor Rutherford suggested the possibility of using an ionized gas for this purpose. He had previously shown that the ionization current, through a gas subject to a constant source of ionization, was approximately proportional to the potential difference between the plates when this potential was small. The writer has used this principle successfully for the past three years, and is satisfied that it gives as accurate results as any of the rate methods. It is also much less troublesome, when it is once arranged, and is adapted to measurements for which the other methods are unsuited. It should be mentioned here that recently J. S. Allen (Phil. Mag., Dec., 1907) has described a zero method for the measurement of ionization currents, which also avoids some of the difficulties of the rate methods.

The standard testing vessel, as it is called, has gone through quite an evolution during the past three years. The one at present in use is shown in Fig. 2. The shaded portion is ebonite, the electrodes are of aluminum, and the active material consists of about a tenth of a milligram of radium bromide. In general, the relation between the ionization current in such a vessel and the potential difference between the plates is not linear, but depends upon the nature of the active material used, the kind and amount of insulation, and the distance between the plates. However, it is generally possible to so adjust the distance

between the plates that a linear relation will exist for a considerable range of potential. Nevertheless, it is necessary to get a calibration curve for every such vessel. This can only be done by some form of the rate method, which must ultimately be the basis of all such measurements. However, in the case of a calibration curve, the rate method is used under the most advantageous conditions.

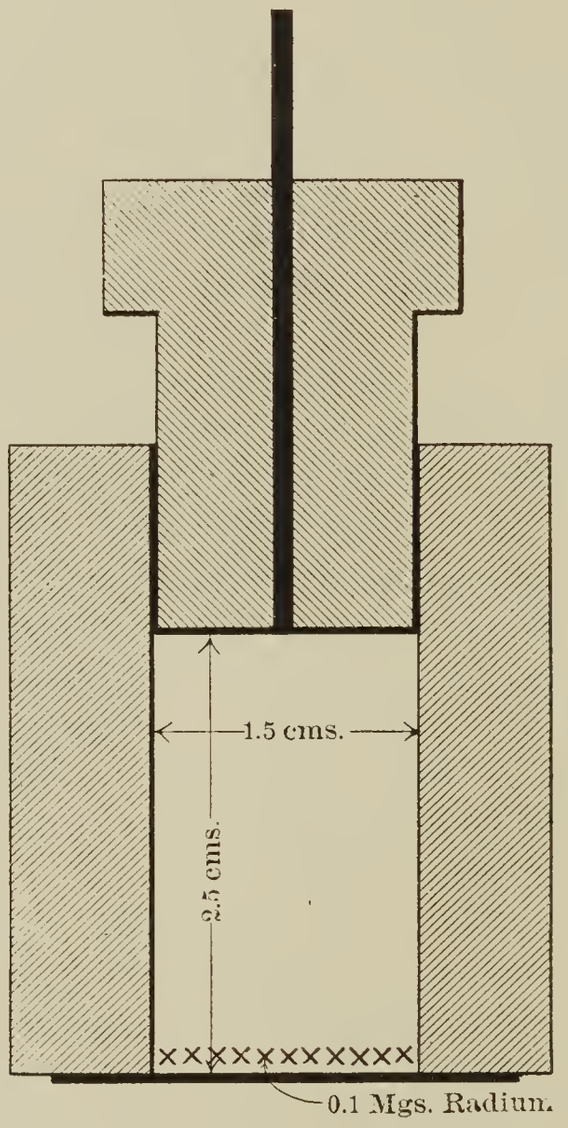

FIG. 2.

Even under these favorable conditions, there are many difficulties which are not easily overcome. This is not surprising when it is remembered that the standard testing vessel has a resistance from 10 to 100 times as great as the values usually given for the resistance of condensers. In calibrating the standard, the condenser is put in place of the testing vessel of Fig. 1 and the system is charged through the standard vessel.

In order to eliminate as far as possible any leakage from the electrometer and condenser, the average potential during the time of charging is kept about zero, and the total change of potential of the system is never more than 0.2 volts. The error due to absorption by the ebonite of the standard is not very large and can be largely eliminated by applying the potential to the standard a few minutes before taking a measurement. In order to calibrate the standard over a considerable range of voltage, for example, from 100 to 0.1 volts, and at the same time not have too great a change in the rate of movement of the electrometer needle, it is necessary to change the capacity of the system. The accurate comparison of these capacities offers the greatest difficulty to the calibration. The writer used a subdivided mica condenser, the sections having capacities from 0.5 to 0.001 microfarads. Several methods were used in calibrating this condenser. The different methods gave very concordant results for the larger sections, but gave values for the smaller sections which differed in some cases by more than 10 per cent. from one another. There is the added difficulty in the use of these small capacities that the potential on the standard is also small. Thus, with one volt on the standard, a change of 0.2 volts in the potential of the quadrants will change the potential on the standard by 20 per cent.

It has, therefore, been found advisable to use a double method of calibration. If we have some radio-active material whose rate of decay has been accurately determined (which, of course, originally involved the rate method), we can use this rate of decay as a means of calibration. The active deposit from actinum is probably the best substance for this purpose, as its rate of decay has been carefully determined by a number of observers and their results agree very well. The following are some of the best values of the time taken for it to decay to half-value:

Godlewski	36 minutes
Meyer and Schweidler	35.8 minutes
Hahn and Lochur	36.4 minutes
Debierne	36 minutes

If we take 36 minutes as the mean value, it cannot be far from the truth.

Fig. 3, curve A, represents the logarithmic decay curve of the active deposit of actinum, as measured by one of the standard vessels. The ordinates represent time in minutes, and the abscissæ the log. of the voltages on the standard. The straight line, B, represents the relative values of the ionization current

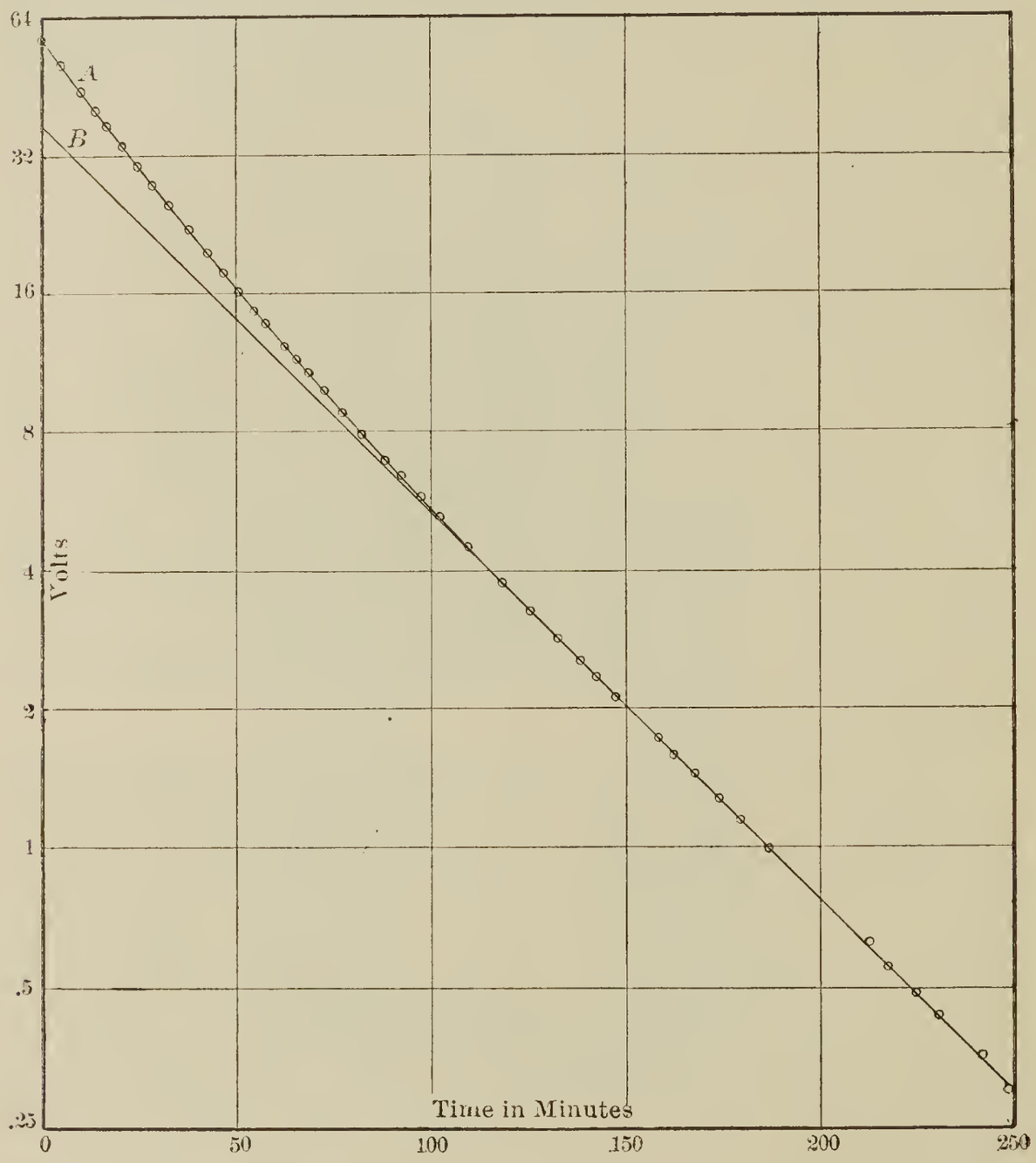

Fig. 3.

at the different times, on the assumption that the active matter decayed to half-value in 36 minutes. If the current through the standard vessel were proportional to the potential difference between its plates, then curve A would coincide with B. It is evident, from the figure, that the potential increases more

rapidly than the current; that is, the apparent resistance of the standard begins to increase when its voltage rises above about 5 volts. The ratio of the abscissæ of curves A and B at any time is a measure of the resistance of the standard vessel for that voltage. If we thus compare the resistances at 20, 40 and 60 volts, we find their ratio to be 1 : 1.16 : 1.28. In order to verify these values, the actual current through the standard for the voltages was measured by the condenser and rate method. The actual resistances were found to be 0.971×10^{11}, 1.14×10^{11} and 1.25×10^{11}. The ratio of these resistances is 1 : 1.17 : 1.28. We thus see that the two methods agree when fairly large voltages and capacities can be used. For the smaller currents, the use of a decaying radio-active substance is much the best method.

The results given in this paper would suggest the possibility of making of standard vessels, similar to the one here described, and preserving them as permanent high resistance standards. They would have a much higher resistance than any standards with which the writer is acquainted, and ought to remain constant over a long period. They would be found very useful for insulation testing or any very high resistance measurements.

Since writing the above, a paper by G. W. Stewart, on "A Satisfactory Form of High Resistance," has appeared in the April number of the "Physical Review." The resistances with which he experimented were not over three megohms, and the results which he obtained with these, such as constancy for all voltages and permanency, would not necessarily apply to resistances 100 times as large, even if similarly constructed. The writer's experience has been that all the difficulties increase very rapidly as the resistances are made larger.

McGill University, Montreal,
April 15, 1908.

DISCUSSION.

Dr. F. A. Wolff: A standard suitable for the measurement of resistances of the order of magnitude mentioned will be gladly welcomed, even though its value is a function of the test

current, particularly as it would make practicable zero and steady deflection methods where now the rates of charge and discharge are directly employed. It may be interesting to note that a further application of ionizing has recently been proposed to a different field by Prof. Richarson, of Princeton, who has found that high temperatures may be measured by the rate at which an electrical charge is dissipated by hot bodies.

Mr. Carl Hering: It seems a rather radical departure to use gas as a conductor, but the results seem to warrant it. I was interested to see that such resistances were really permanent and reliable. The question of whether such a resistance is reproducible does not seem to be of importance, because, as I understand it, each one must be calibrated after it is made. The question arises, can they be adjusted to any fixed value?

Concerning the changing of graphite resistances, I can confirm the fact that a graphite line on ground glass is very unreliable. I had occasion to experiment with these some twenty years ago; resistances of several megohms were made in this way, but we came to the same conclusion that the resistance was really mainly an accidental ore, a mere contact resistance; it was very unreliable and apt to change.

Concerning the use of electrolytes as resistance, I think the so-called reststrom of Helmholz, would make a difference between the apparent and the real resistance.

Concerning the measurement of extremely small currents, I might call attention to an observation made by Dr. Northrup and myself some years ago, while experimenting with the Brownian movements. We noticed that when very small suspended particles were seen under the microscope (such as those showing the Brownian movements), if a current was passed through the liquid, there was a very marked and decided movement of the particles either in the direction of, or in the opposite direction to, the current. The movement was so decided and seemed to respond to the current so accurately that it occurred to Dr. Northrup that such a method might be used for measuring extremely small currents. We noticed that the moment a current was started, these particles, which did not seem to have any appreciable inertia, started moving instantly, and the moment the current was stopped they stopped instantly. Of course, they had their other move-

ments also, but those are quite different from the movements due to the current. The stronger the current the more rapid the movements. With relatively strong currents, the movement was so rapid that the particles flew across the field of the microscope, so that you could see nothing but a streak, and at other times it was so slow that we could time the velocity. What the currents were in amperes we cannot say, but I should imagine they were well down in the micro-amperes, and if that is the case, this method might perhaps be used for measuring extremely small currents. There is one disadvantage in it, and that is the particles will also move across the field due to electrification, when there is assumed to be no current passing. We found them moving through what are supposed to be insulating liquids, between two plates which were electrified. This is, therefore, a case in which presumably no current was flowing, and yet the particles moved, but possibly they moved because some slight current did actually flow even through a supposed insulator.

Prof. W. D. Bancroft: Does the gas in the enclosed vessel have any effect? It seems quite possible that under the influence of the radium salt, oxygen would in time react either with the aluminum or with the ebonite walls, and the question at once arises—would that have any effect on the internal resistance?

Mr. Bronson: Dr. Bancroft's question raises a very interesting point, which will require observations over a considerable length of time before a definite answer can be given. The measurements, which I have made by means of the standard testing vessel, have only been relative ones, which only extended over a few hours. The question of absolute permanency was, therefore, unimportant, and I have neglected to investigate it carefully, but shall try to do so in the near future.

A lecture delivered at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., April 30, 1908; President C. F. Burgess in the Chair.

THE ELECTROCHEMISTRY OF LIGHT.

By Wilder D. Bancroft.

The first generalization as to the chemical action of light was that the light was converted into heat and that the action was due to heat. This hypothesis was supported by Gay-Lussac and Thénard and by Rumford, but it did not prove tenable. Light will decompose a solution of mercuric chloride and ammonium oxalate in water though this solution is not changed by boiling in the dark. If the heating effect were the sole one, we should expect silver bromide to be decomposed more readily by the longer waves than by the shorter ones. Light converts oxygen readily into ozone, but it is a rather hopeless task to get appreciable quantities of ozone by heating oxygen.

Other less ambitious generalizations have been to the effect that inorganic compounds are reduced by violet light and oxidized by red light or that organic compounds are oxidized by violet light. These have not proved satisfactory and their inherent futility has been pointed out by Oswald.[1] The result is that the books on photochemistry consist of a mass of empirical facts. The surprising thing about all this is that for ninety years there has been in existence a theory of the chemical action of light which would have brought order out of chaos if anybody had taken it seriously. This theory was not the work of an unknown man; it was by Grotthuss, the man who gave the explanation of electrolytic action which held the stage for many decades. The success of Grotthuss' explanation of electrolytic action makes it all the more surprising that people apparently did not take seriously his explanation of photochemical action.

In 1818, Grotthuss[2] published a paper on the chemical action of

[1] Lehrbuch allgem. Chem., 2d Ed., 2 I, 1083.

[2] Ostwald's Klassiker, 152, 104, 115.

light in which he put forward what should be known as the first two laws of photochemistry. The first law is that only those rays which are absorbed can produce chemical action. This does not mean that all rays which are absorbed do produce chemical action. This law was rediscovered by Herschel and by Draper and is often known as Herschel's law or as Draper's law.

The second law of photochemistry is that a ray of light acts like a linear voltaic cell. Now it may be a question just what Grotthuss meant by this, but it is only right to give Grotthuss the benefit of any doubt, and I interpret it as meaning that the chemical action of light is the same as the electrolytic action in case one did or could electrolyze the system, all the other conditions remaining the same. My object is to show you the way in which the theory of Grotthuss applies to a large number of cases, and I hope to convince you that it is only our insufficient knowledge of chemistry and of electrochemistry which prevents our applying it to all cases.

The theory of Grotthuss aims to tell us what the chemical action of light will be. One word as to the way in which the light acts may not be out of place. Light, which is absorbed by a system and which is not converted into heat, must be used to increase the chemical potential if we are dealing with a system in which the varying intensity factors are the temperature, the pressure, and the chemical potentials. Putting the system under an electrical stress also raises the chemical potentials and the theory of Grotthuss is merely another way of saying that we get the same chemical reactions as a result of increasing the chemical potentials in these two different ways. In the case of reversible reactions which can be arranged to produce electrical energy, we know that light changes the electromotive force and therefore the chemical potentials. It may be urged against this explanation that heat also raises the chemical potentials by raising the temperature and that the reactions produced by heat should therefore be identical with those produced by light or electricity. I am quite ready to admit the force of this argument because I believe that it accounts for the parallelism between the effects of light and of heat which certainly does exist in a great many cases. I am now collecting data for a possible paper on "The Electrochemistry of Heat," in which I hope to show that the action of heat, electricity and

light is the same except when we are dealing with selective effects.

Under favorable conditions, salts of many of the metals are changed by light. Light-sensitiveness has been observed with salts of silver, gold, the platinum metals, mercury, copper, lead, tin, iron, nickel, cobalt, chromium, cerium, molybdenum, manganese and vanadium, not to mention others. It is not true, however, that all the salts of all these metals are sensitive to light. If we consider the action of light as equivalent to that of a low voltage current, we see that we shall get decomposition only in presence of a suitable depolarizer. For instance, ferric chloride in aqueous solution is practically not reduced by light, because the reduction products, ferrous chloride and chlorine, would recombine promptly. In alcoholic solution, ferric chloride is reduced by light because alcohol is a depolarizer for chlorine. An alcoholic solution of ferric sulphate is only reduced very slowly by light because alcohol is a poor depolarizer for sulphate. In the case of ferric oxalate we have a readily decomposable anion and ferric oxalate is consequently readily reduced by light. Mercuric oxalate is even more readily reduced by light. Gelatine reacts with bromine and acts therefore as a depolarizer or "chemical sensitizer" for silver bromide. The chromates and the manganates are reduced by light only in presence of organic matter, and the reduction of uranyl salts to uranous salts takes place only in presence of a depolarizer. In all these cases the action of light is the same as the cathodic reduction. One very satisfactory instance of this is to be found in Fehling's solution from which cuprous oxide precipitates on exposure to light while we get cuprous oxide at the cathode if we electrolyze the solution.

Just to illustrate the principle we have made a number of what I may call electrolytic photographs. The letter C, for Cornell, was cut out in silver or in copper, laid upon a photographic paper, and made cathode for a few moments while a very small current passed. In this way we get an image of the cathode and I have here some samples of electrolytic silver prints, electrolytic blue prints and electrolytic cuprous oxide prints. I call your attention to one difference between the electrolytic photographs and the sun photographs. Slight inequalities in the surface of the photographic paper make no difference in the case of a real photo-

graph because the rays of light keep on until they strike the paper. If any portion of the paper, however, does not come in contact with the metal cathode, there will be no reduction at that point and there will be white spots in the print, as is shown in some of the samples I have here.

In all these cases the action of light is wholly or in part a reducing one; but this is not always so. A very striking instance was studied by Grotthuss himself. A red solution of ferric sulphocyanate in alcohol is bleached by sunlight, which is as it should be. If left in the dark, the solution absorbs oxygen and becomes red again, which is also as it should be. If, however, the solution, in a tall stand-glass, is left in the window for twenty-four hours, it will be red at night, colorless during the early morning, red at noon, colorless in the afternoon and red again at night. This unexpected cycle of changes seemed to indicate a difference between the sunlight of the morning and afternoon and that of the noon period. Grotthuss showed, however, that the different effects depended on the height of the sun and the shape of the vsssel in which the solution stood. In the morning and the afternoon the sun's rays are nearly horizontal in North Germany, and they therefore passed through the glass of the containing vessel into the solution. When the sun was more nearly overhead, as at noon, the rays passed directly from the air into the solution. To show that the combination of sunlight, air and solution caused oxidation, Grotthus reflected light up through the bottom of the vessel so that the light passed from the solution to the air instead of from the air to the solution. Oxidation took place as before.

This set of experiments by Grotthuss gives us the clue to the conditions under which we get reduction or oxidation by light. The chemical effect of the light is merely to eliminate if possible the substance absorbing the light. Whether that elimination takes place as a result of oxidation or if reduction is a matter which is quite independent of the light and which depends entirely on the nature of the depolarizer. If the depolarizer is a sufficiently strong reducing agent, we get reduction by light. If the depolarizer is a sufficiently strong oxidizing agent we get oxidation by light. If it is not sufficiently one or the other, we get no action by light. A very good instance of the variable action of light is to be found in the case of mercurous chloride. In the

presence of a sufficiently powerful reducing agent, light reduces mercurious chloride to metallic mercury. In the presence of a sufficiently powerful oxidizing agent, light oxidizes mercurous chloride to a mercuric salt. If there is no more suitable depolarizer present, the mercurous chloride itself acts as a depolarizer and is changed by light to mercury and mercuric chloride. These changes can, of course, all be duplicated electrolytically.

In some cases the action of light appears to be quite different from that of electrolysis. If an aqueous solution of oxalic acid be saturated with air and exposed to sunlight, the reaction products are hydrogen peroxide and carbon dioxide.

$$H_2C_2O_4 + O_2 = H_2O_2 + 2CO_2.$$

The normal products of electrolysis are water and carbon dioxide:

$$H_2C_2O_4 + O = H_2O + 2CO_2.$$

If we electrolyze between platinum black electrodes saturated with oxygen, we shall get carbon dioxide at the anode as before. At the cathode, however, we have what Traube[3] has shown to be the ideal conditions for getting a quantitative yield of hydrogen peroxide. Light and electrolysis, therefore, do give the same reaction products when the conditions correspond.

It was shown by Fay[4] that the action of sunlight on a solution of propionic and uranyl nitrate forms ethane and carbon dioxide chiefly:

$$CH_3CH_2CO_2H = CH_3CH_3 + CO_2.$$

With acetic acid and uranyl nitrate the chief products are methane and barbon dioxide:

$$CH_3CO_2H = CH_4 + CO_2.$$

There is also a precipitation of uranium salt, but I am inclined to think that is irrelevant. Jahn[5] showed that the electrolytic

[3] Ber. Chem. Ges., Berlin, **15**, 2434 (1882).

[4] Am. Chem. Jour., **18**, 269 (1896).

[5] Wied. Ann., **37**, 430 (1889). *Cf.* Petersen, Zeit. phys. Chem., **33**, 111 (1900). (1900).

decomposition products of sodium propionate under certain conditions were ethylene, carbon dioxide and hydrogen:

$$CH_3CH_2CO_2H = CH_2CH_2 + CO_2 + H_2.$$

Now in electrolysis the anode products are formed in one place and the cathode products in another. In the case of reactions caused by light the anode products and the cathode products are set free at the same place and therefore may interact with each other. If the ethylene and the hydrogen of the electrolytic action combine to form ethane, we have then the decomposition products due to the action of light. One way to realize this experimentally would be to use an alternating current. We have not yet tried this propionic acid; but we have with acetic acid.

The ordinary electrolytic decomposition products of aqueous sodium acetate are ethane, carbon dioxide and hydrogen:

$$2CH_3CO_2H = C_2H_6 + 2CO_2 + H_2.$$

If the nascent hydrogen were evolved at the point where the acid radical was breaking down, it is quite conceivable that the CH_3 group would combine with the hydrogen instead of polymerizing. When a calcium acetate solution was electrolyzed with an alternating current and a high current density, no ethane was formed and some methane was evolved. Unfortunately the chief reaction is an oxidation of the acetic acid so that the yield of methane is not high.

While we cannot yet regulate the conditions so as to make methane the chief electrolytic decomposition product of acetic acid, we can effect this decomposition in another way by heating calcium acetate with lime.

$$Ca(CH_3CO_2)_2 + CaO_2H_2 = 2CaCO_3 + 2CH_4.$$

If we heat calcium acetate by itself, the main reaction is:

$$Ca(CH_3CO_2)_2 = CaCO_3 + CH_3COCH_3.$$

Of course, we do not know that the acetone formation is an intermediate step in the methane formation and I cannot find any record that any organic chemist has ever converted acetone into

methane by heating with lime. We know, however, that it is easy to oxidize acetone to acetic acid and formic acid. In view of the behavior of calcium acetate and lime, it seems possible that we might have the following reactions if we eliminated oxidation:

$$CH_3COCH_3 + CaO_2H_2 = Ca\begin{matrix} OH \\ CH_3CO_2 \end{matrix} + CH_4.$$

$$Ca\begin{matrix} OH \\ CH_3CO_2 \end{matrix} = CaCO_3 + CH_4.$$

Eliminating the calcium oxide from the reaction we have:

$$CH_3COCH_3 + H_2O = CH_3CO_2H + CH_4 = 2CH_4 + CO_2.$$

The conversion of acetone into acetic acid and methane takes place slowly in sunlight.[6] The second change from acetic acid into methane and carbon dioxide takes place in the sunlight in the presence of uranyl nitrate, and doubtless under other conditions. The conversion of acetic acid into marsh gas and carbon dioxide can also be effected by ferments. These light reactions are therefore not exceptional ones as has sometimes been claimed. They can be duplicated in some stages, and perhaps in all by the action of heat. They can be duplicated to a certain extent electrolytically and could be duplicated exactly if it were possible to eliminate oxidation. Consequently the action of light is the same as the action of the electrolysis when the disturbing factors are eliminated.

Some interesting parallels between the action of light and of electrolysis are to be found in the blue print processes studied by Herschel,* in 1841. If we impregnate a piece of paper with an ammonium ferric citrate solution and a potassium ferricyanide solution, sunlight will change the ferric citrate to a ferrous salt and we get a blue image composed of ferrous ferricyanide. If we expose the paper a long while to an intense light, the blue image becomes white because it is changed into ferrous ferrocyanide. On still longer exposure the white image becomes brown. It does not seem to be known just what this brown compound is, though

[6] Ciamician and Silber, Ann. Chim. Phys. (8) **11**, 433 (1907).
* Phil. Trans., **132**, 201 (1842).

it may have the formula[7] $KF_2(CN)_5$. For our purposes it is immaterial what the substance is. The important point is that the continued action of light gives us a blue image, a white image, and lastly, a brown image, and that these three changes to blue, white and brown can be duplicated electrolytically. There is the possibility of a very pretty experiment here, though I must confess that it works better on paper than in practice. Suppose we get a white image electrolytically and wash out the unchanged salts without letting the ferrous ferrocyanide oxidize. We shall then have the beautifully artistic effect of a white image on a white ground. To show that there really is an image we can flow the paper with a hydrogen peroxide solution when the white ferrous ferrocyanide will be oxidized to a deep blue. The weak point about this is that the ferrous ferrocyanide always oxidizes a little in the air and one consequently has a pale blue image instead of a white one.

In the formation of the white image by light it seems natural to suppose that the light reduced the ferricyanide to ferrocyanide and this is the more plausible because light will reduce ferricyanide to ferrocyanide. Herschel showed, however, that the reaction proceeded in a different way under these circumstances. He saturated with ammonium ferric citrate alone and exposed it for a long time to light. On pouring a potassium ferricyanide solution over the paper a white image was formed, showing that the decomposition of the ferric citrate yielded a product which would reduce potassium ferricyanide. We have electrolyzed a citric acid solution and have found that the anode liquor contains a substance, probably formic acid, which reduces potassium ferricyanide solution to potassium ferrocyanide. The two sets of reactions are therefore identical.

An interesting problem comes up in the oxidation of dyes in the light. It has been suggested that the oxidation is really caused by ozone, and this is not impossible because ultra-violet light will change oxygen into ozone. The theory of Grotthuss enables us, however, to answer the question. If the active light is the light which is absorbed by the dye, then it is the dye that is made active and the oxygen which acts as a depolarizer. Actual experiment shows that in almost all cases the active rays are those

[7] Roscoe and Schorlemmer, 2, II, 107 (1886).

which are absorbed by the dye. This disposes of the ozone theory as the important factor though, of course, there may be some oxidation by ozone. While the gas is apparently the depolarizer in this case, this is not always so. When chlorine reacts with silver or bromine with toluene, the active light is the light absorbed by the halogen.

If we stain a photographic plate with eosine or erythrosine we find an increased sensitiveness for the yellow-green rays. This brings up two questions. For what rays do we get the increased sensitiveness and how do these so-called "optical sensitizers" act? The first experiments by Vogel and by Eder showed that the maximum sensitizing action on the plate did not coincide exactly with the maximum absorption of the dye in aqueous or alcoholic solution. This was not surprising, because it is well known that the position of the absorption bands varies with the solvent. Eder[8] therefore stained pure silver bromide and showed that then those rays produced the maximum sensitizing action which were the most absorbed by the stained silver bromide. This would seem to be conclusive; but Acworth[9] raised the point that both sets of measurements should be made on an actual photographic plate. At first sight that seems the proper thing to do; but when Acworth made the measurements, he found that the maximum sensitizing action was further toward the red end of the spectrum than the maximum absorption and he therefore put forward a mathematical theory to show that this must be so. Now one great beauty of many mathematical theories depending on vibratory molecules is they can be made to account for any facts which happen to be known at the time. The disadvantage about them is that they will account for an inaccurate observation just as well as for an accurate one. Their actual value is therefore usually small.

The conclusions of Acworth seem to be accepted by some people even now,[10] and therefore the error in them must be pointed out. A photographic plate is not homogeneous. It consists of an emulsion of gelatine and a silver salt or salts, chiefly silver bromide. Eosine stains both the gelatine and the

[8] Ber. Akad. Wiss., Wien, **92**, II, 1368 (1885).

[9] Wied. Ann., **42**, 371 (1891).

[10] Ostwald, Lehrbuch allgem. Chemie, 2d Ed., **2**, 1, 1060; Byk, Zeit. phys. Chem., **62**, 488 (1908).

silver bromide, but the gelatine a good deal more than the bromide. As far as the optical absorption is concerned, the dye in the gelatine will count for a good deal more than the dye in the silver bromide. As far as the sensitizing effect is concerned, only that dye which is in contact with the silver bromide can be effective. In the absorption experiments Acworth measured the sum of the absorption due to the stained gelatine and the stained silver bromide, the latter absorption being pretty well masked by the former. In the sensitizing experiments Acworth measured the effect due to the stained silver bromide and his two sets of results could not possibly coincide. An illustration will perhaps help. The absorption spectrum of iodine in benzene differs from the absorption spectrum of iodine in water. If we add iodine to a mixture of benzene and water, most of the iodine goes into the benzene.[11] If we determine the absorption of light which has passed through both layers, we shall get an absorption spectrum which will not differ perceptibly from that of iodine in benzene. If, however, the iodine were light-sensitive in water, reacting with it, and not light-sensitive in benzene, it would be the rays that were absorbed by the aqueous solution that would count photochemically and not the others. Substitute gelatine, silver bromide and eosine, respectively, for benzene, water and iodine, and we get the actual facts, except that the eosine is also light- sensitive in gelatine.

The next question is as to the way in which the sensitizers act. According to the theory of Grotthuss, they must be depolarizers. It would be more in line with the previous use of the word depolarizer to say that silver bromide must be a depolarizer for the sensitizers; but that is of minor importance. Under the influence of light, the sensitizers must either reduce silver bromide directly or must be changed by light into a substance which does reduce silver bromide. Since eosine and erythrosine contain large amounts of bromine and iodine, respectively, it was not to be expected that they should take up bromine directly from the silver bromide. If they were to act in that way it would be reasonable to expect fluoresceine to be a better sensitizer, which is not the case. They might, however, act as bromine carriers by giving

[11] The amount of iodine going into the benzene can be varied by adding alcohol to the solution.

up a portion of their own halogen to the gelatine and then taking up bromine from the silver bromide. If this is the case, the action of light on an eosine solution should set free halogen and we have shown experimentally that this is the case. A very striking and conclusive experiment was performed by Abney, who stained a gelatine film with cyanine, exposed it to the solar spectrum, added silver bromide after the exposure, and developed. An image was obtained at the points corresponding to the rays absorbed by cyanine. Cyanine was therefore changed by light into a substance which reacted subsequently with silver bromide. Abney believed that the cyanine was oxidized, but this is disproved by an experiment of Bothamley's, in which he showed that sensitizers were effective even when the plate is submerged in a pyrogallol solution. We have tried to duplicate Abney's experiment, using eosine instead of cyanine; but we have been unsuccessful because the reduction product apparently reacts in other ways before it can be brought in contact with the silver bromide. This is not surprising because it has been shown by others that eosine will absorb oxygen when exposed to sunlight[12] and that it will even act as an oxygen-carrier.[13]

Since sunlight causes chlorine or bromine to react with benzene or toluene, it acts as a halogen carrier and we must therefore consider the theory of halogen carriers. Speaking roughly, the general action of some of the halogen carriers in the chlorination of toluene is shown in Table I.

TABLE I.

Sunlight	Substitution in side-chain.
Electrolysis	Substitution in ring.
$SnCl_4$	Substitution in ring.
Fe_2Cl_6	Substitution in ring.
Al_2Cl_6	Substitution in ring.
ICl	Substitution in ring.
PCl_5	Substitution in side-chain.
H_2O	Substitution in side-chain.

This is not absolutely accurate. Electrolysis will give side-chain substitution under some circumstances and water will give some

[12] Gros, Zeit, phys. Chem., **37**, 157 (1907).
[13] Straub, Archiv exp. Path. und Pharm., **51**, 383 (1904).

ring substitution. Bromine and toluene give ring substitution in sunshine under some circumstances and we get side-chain substitution with ICl if the temperature is high enough or the concentration of ICl low enough. In this paper I am ignoring all these points which will be taken up in detail in a paper on halogen carriers which will appear in the June number of the *Journal of Physical Chemistry* and in an experimental paper by Mr. Schluederberg which will appear in the autumn. In this paper I am merely touching the high points. Whatever is said about ring and chain substitution with toluene applies pretty closely to substitution and addition products in the case of benzene.

The first thing to be noticed about Table 1 is the marked difference between the action of light and that of electrolysis. This must be due to a difference somewhere in the conditions. Now we know that ultra-violet light causes gases to conduct and the simplest assumption is that we have a partial dissociation into something positive or negative. It is immaterial what these products are. They may be ions or they may be some other abstraction. It is only necessary that they should be positive and negative and that they should be capable of at least a temporary existence. For the sake of convenience we will call them gaseous ions without, however, committing ourselves to any definite conception thereby. We will also make the explicit assumption *ad hoc* that ring substitution takes place when we have an excess of negative ions and chain substitution when this is not the case. In the case of chlorine and sunlight, we have an equilibrium.

$$Cl_2 \leftrightharpoons Cl^+ + Cl^-$$

and we have side-chain substitution by definition. In an aqueous hydrochloric acid solution we have chlorine anions and these, when set free electrolytically, will give us negative chlorine at first and therefore ring substitution. If the efficiency is less than one hundred per cent., we shall get some of the negative chlorine changing over into positive chlorine as a preliminary to the formation of chlorine gas. This gives us favorable conditions for side-chain substitution and Mr. Schluederberg has obtained some side-chain substitution electrolytically.

With stannic chloride we have a strongly metallic basic radical and we shall have an equilibrium represented by the equation

$$SnCl_4 \leftrightharpoons SnCl_2 + 2Cl^-.$$

With stannic chloride and ferric chloride we should expect to get ring substitution exclusively and that is what we have. By the time wet get to iodine monochloride it is rather a toss-up whether we are going to have negative chlorine or positive chlorine; but we do get ring substitution in most cases. With phosphorus pentachloride we are apparently across the line because we get side-chain substitution. The equilibrium is therefore written

$$PCl_5 \leftrightharpoons PCl_3 + 2Cl^+.$$

Water acts as a carrier both for benzene and toluene. It is the best carrier if we wish to make benzene hexabromide. We are familiar with the reversible equilibrium

$$C_2 + H_2O \leftrightharpoons HC + HCO.$$

To account for the action of water as a carrier we have merely to postulate the intermediate stage

$$Cl_2 + H_2O \leftrightharpoons Cl^+ + Cl^- + H_2O \leftrightharpoons HCl + HClO.$$

There are some apparently weak points about this argument. One of them is that we postulate ferric chloride as the active agent and it is usually stated that ferric chloride will not be reduced by benzene or toluene. Mr. Schluederberg has shown, however that this statement is not correct. The reaction takes place vigorously at about 60° under the influence of sunlight.

A second apparently weak point is that we postulate the existence of an aluminous chloride, whereas no aluminous salts are known. Mr. Turrentine has shown, however, that hydrogen is evolved at the anode when aluminum is made anode in a chloride solution and there is a high anode current density. This is due to the formation of an instable salt of aluminum which reacts with water and evolves hydrogen. While aluminous chloride has not yet been isolated, its temporary existence in the solution has been demonstrated, which is all that is necessary for the present.

This hypothesis as to the way in which halogen carriers act has the advantage that it accounts for the reaction velocity equations

in a way that no other explanation does. Since the general reaction with benzene and with toluene is

$$C_6H_6 + 2Cl^+ = C_6H_5Cl + HCl.$$
$$C_6H_5CH_3 + 2Cl = C_6H_4ClCH_3 + HCl$$

the following equations represent the necessary equilibria

$$2ICl \leftrightharpoons 8I^+ + 2Cl^-$$
$$SnCl_4 \leftrightharpoons SnCl_2 + 2Cl^-$$
$$Fe_2Cl_6 \leftrightharpoons 2FeCl_2 + 2Cl^-$$
$$Al_2Cl_6 \leftrightharpoons 2ClCl_2 + 2Cl^-.$$

In other words the reaction velocity will be proportional to the square of the concentration of the iodine monochloride and to the first power of the concentration of the stannic chloride, the ferric chloride, or the aluminum chloride. This is exactly what has been found experimentally.

These illustrations give an idea of the usefulness of the theory of Grotthuss in the cases in which we have formation or decomposition of compounds. It is necessary, however, to account for the allotropic changes produced by light. As typical cases we will consider oxygen, phosphorus and sulphur—with a reference to anthracene. Oxygen is converted into ozone by ultra-violet light of certain wave-lengths. We can also get ozone electrolytically and it is only our ignorance of all the conditions affecting the electrolytic production of ozone which prevents our going into the matter in more detail. In the case of phosphorus, light changes the instable form into the stable form and that is just what the current would do if we could arrange an electrolytic cell with phosphorus electrodes and an electrolyte from which phosphorus would be precipitated at the cathode electrolytically. The case is analogous to the behavior of the two forms of tin when short-circuited in a solution of a tin salt.

The case of sulphur is different from that of phosphorus because light causes the formation of an instable form, insoluble sulphur so-called. Berthelot[14] has solved the problem for us. He showed that soluble sulphur precipitated at the anode if a solution of hydrogen sulphide were electrolyzed and that insoluble sulphur was formed at the cathode during the electrolysis of solutions of

[14] Ann. Chim. Phys. (3) **49**, 448 (1857).

sulphuric or sulphurous acid. In fact, Berthelot called the insoluble sulphur electropositive sulphur and the soluble sulphur electronegative sulphur. While not able to agree that the sulphur at the cathode is entirely insoluble sulphur, the fact remains that we can change insoluble sulphur electrolytically into soluble sulphur and that the reaction produced by light can therefore be duplicated electrolytically. It may be asked why the insoluble form of sulphur should precipitate at the cathode and the instable form of oxygen at the anode. I am not able to answer that question satisfactorily now; but I should like to call attention to the following facts. In the oxygen-ozone equilibrium both reactions can be accelerated by light while we do know that that is the case for sulphur. Sulphur can conceivably be a cation; but it is difficult to see under what circumstances oxygen could be. Mr. Turrentine has succeeded in getting ozone at the cathode during the electrolysis of an acidified permanganate solution. While the ozone in that case was undoubtedly the result of a secondary action, yet the fact of its appearance at all is not without interest.

The last case is that of anthracene which is converted by light into dianthracene. I cannot tell how this change can be brought about electrolytically because we have been too busy with halogen carriers to make any experiments at all with anthracene. I recognize, however, that it is obligatory upon me to work out the process unless some one else does it first. By next year I hope to be able to effect the conversion electrolytically. It is interesting to note that Byk[15] has recently discussed the theoretical possibility of making dianthracene from anthracene by means of an alternating current. Unfortunately, he also has made no experiments as yet.

When quoting the first law of photochemistry, I said that all rays which are absorbed do not necessarily cause chemical action. A very remarkable case of this is to be found in the action of bromine on toluene. The absorption of light by bromine is much more marked in the greenish-blue and the blue than it is in the yellow-green and the orange; but it is the rays corresponding to the latter absorption which are most effective in bringing about the reaction between bromine and toluene.[16] Byk[17] cites an-

[15] Zeit. phys. Chem., 62, 478 (1908).
[16] Schramm and Zakrzewski.. Monatsheft, 8, 299 (1887).
[17] Zeit. phys. Chem., 49, 681 (1904); 62, 487 (1908).

other case of the same sort. Fehling's solution has an absorption band at the red end of the visible spectrum and another in the ultra-violet. It is the rays corresponding to the latter absorption band which cause the precipitation of cuprous oxide. We get something similar in the fluorescent solutions where some of the absorption bands do not correspond to exciting rays. It seems hardly probable that these inert absorption bands, if I may use such a phrase, are intended solely for beauty. I have the feeling that the light corresponding to them must be active in producing some other chemical reaction. If this be true, it opens up a possibility of connecting absorption bands and structure formulas in a most fascinating way. A beginning has apparently been made by Baly and Collie,[18] who have found that benzene has seven absorption bands and that each absorption band corresponds to some definite change. This indicates a possibility of perhaps preparing any desired di-substituted compound by using light of the right wave-length. For the moment, however, this is only a speculation.

There are many applications of the theory of Grotthuss but it will take time to work them out. Some of the subjects with which I hope to deal later are: Oxygen carriers, solarization; conductivity of gases; fluorescence and phosphorescence; chemiluminescence. In the still more remote future we see the whole question of plant growth and animal physiology, problems to a great extent of photo-chemistry. When one stops to think of it, photochemistry, if taken in a broad sense, is one of the most important and least developed branches of chemistry. The guiding principle which will enable us to develop this vast and important field is the one enunciated by Grotthus, in 1818, that the action of light is analogous to that of a voltaic cell.

Cornell University.

DISCUSSION.

President Burgess: Dr. Bancroft, you have the thanks of the society for your interesting lecture. The subject is open for discussion.

[18] Jour. Chem. Soc., **87**, 1332 (1905).

Dr. L. H. Baekeland: Physical chemistry has given us the means to convince ourselves that chemical reactions, however simple they may appear at first, are far different from what we used to imagine they were. We are now being led to the evidence that a simple inorganic reaction, for instance the precipitation of an insoluble salt is a far more intricate process than we ever supposed before. All this has rendered us rather skeptical in regard to the easy-going-cut-and-dried theoretical explanations in which we have indulged so long in the field of organic chemistry. In that branch of chemistry it has very frequently occurred that in order to save some pet theory, we neglected in a reaction sometimes as much as ninety per cent. of so-called "side products" to put the main stress on the ten per cent. yield of the substance we were looking for. It was high time to stop such careless superficial research work and physical chemistry is teaching us better manners. I believe that photochemistry even more than electrochemistry may bring about this result as soon as the latter will cease to be so very much neglected by physical chemists. Aside of some splendid work done by a very few able, well-prepared and conscientious experimenters, most of the photochemical literature of to-day presents us a chaos of superficially observed facts, often carried out by men improperly trained for experimental work, sometimes utterly incompetent; their conclusions have quite often been arrived at by confounding coincidence with cause; I refer mainly to the class of work carried out by mere photographers unqualified to make physical or chemical observations of unusual sensitiveness.

Indeed, some photochemical phenomena are of such a delicate nature, so difficult to observe accurately, that in this respect they outrank almost all other chemical reactions. What analytical method, what physical means do we possess to establish a difference between silver bromide before and after it has been submitted to the action of light for a fraction of a second? And yet we know that although its chemical and physical qualities seem unchanged it has acquired suddenly the property of liberating metallic silver as soon as brought in contact with appropriate reducing agents. But we have learned this only by pure accident; were it not but for the experimental worth that was needed for the sake of the photographic arts, we would probably be still

unaware of this remarkable phenomenon, as long as the silver bromide was not altered to the point where its color darkens.

During the late years closer investigation has shown us that several substances are affected by light, but our discoveries have been limited to such cases where this action is easily detected. Who can prove to us that most substances, perhaps all of them, are acted upon by light? A condition of equilibrium may set in in most cases, which forbids the change to progress beyond the very initial stages. Let us find more delicate means than we have been using thus far and we may at the same time discover a hitherto unsuspected field of the greatest magnitude offering increased knowledge as well as useful applications. It is a pity that the attention of photochemists should have been given almost exclusively to the art of making photographs while so many more important problems directly connected with photochemistry have been so badly neglected. To name one of these problems let me remind you that the agricultural prosperity of this and other nations depends mainly on the proper performance of a photochemical reaction: the assimilation of CO_2 by the chlorophyl of the plants under the influence of light. The proper study of this single phenomenon would give us practically the key to the most delicate methods of organic synthesis. Nevertheless, comparatively little work has been done in this direction.

It is not impossible that some day the storage of electrochemical energy may neatly and easily be accomplished by means of a photochemical reaction. Professor Bancroft in his paper has given us many proofs that seem to indicate that there exists a very close relation between electrochemical and photochemical reactions. That photochemical reactions may become reversible has already been abundantly proven. I, myself, some twenty years ago, published the fact that hydrochloric acid under certain conditions undergoes direct oxidation if mixed with air or oxygen and submitted to the action of sunlight. This reaction is the reverse of what occurs when a solution of chlorine in water decomposes and forms hydrochloric acid and oxygen. Permit me to mention also that a few years ago[1] I showed that the latent photographic image may tend to disappear before development. I have given to this phenomenon the name of "Photoretrogres-

[1] Fifth Int. Cong. App. Chem., Vol. IV, p. 403. Berlin, 1903.

sion," and I believe it to be simply a case of reversible photochemical reaction which tends to establish a chemical equilibrium.

As an instance how the most isolated theoretical investigation may sometimes be of immediate practical value, allow me to refer to the cathode images just shown by Prof. Bancroft. One day, in a manufacturing establishment with which I was connected about ten years ago, similar cathode images proved a considerable source of worry and financial loss, and it took me some time to find the cause. White, unsensitive spots occurred on some bromide paper. These spots were so small as to be scarcely visible, but examined under the microscope they consisted of a white zone surrounding an inner smaller nucleus which was black and did not appear unless the surface was scratched away. Careful experimenting and minutious observation revealed the fact that the raw paper contained some microscopic metallic particles imbedded in the mass; these created an electrochemical system in which the cathode zone produced local reduction of silver while the surrounding anode zone became unsensitive and remained white under the action of the developer.[2] I succeeded in producing the phenomenon artificially by using the platinum electrodes of a cell in about the same way as Prof. Bancroft does but carrying out the experiment on a microscopical scale.

PROF. CHAS. BASKERVILLE: A conclusion to be drawn from what has been stated is that light acts practically the same way as the electric current. Am I right?

PROF. BANCROFT: Yes.

PROF. BASKERVILLE: I think it was Weigert, who, in a recently published paper, called attention to some of the principles here laid down, namely, that light might be catalytic in its action, or actually influence reactions in such a way as to make them reversible, which is essentially real chemical energy. However, as Dr. Bancroft stated, we do not know exactly what that is. I would like to ask one more question before going on—the change of yellow phosphorus to red phosphorus, the stable form, is that due to ordinary sunlight or ultra-violet light?

PROF. BANCROFT: It is the ultra-violet light in ordinary sunlight. It would go faster the more intense the ultra-violet light.

PROF. BASKERVILLE: Of course it is easier to knit than to

[2] Fifth Int. Cong. App. Chem., Vol. IV, p. 400, Berlin, 1903.

ravel. (Some one in the audience—"you mean ravel than to knit.") Yes, that it what I meant, but still that depends upon which way you look at it. I cannot but feel, having been interested in the subject of ultra-violet light, like repeating a statement, which perhaps may be attributed to Professor Bancroft as occurring in one of our frequent talks about light in general, namely, that ultra-violet light is a mixture of reagents. If we include ultra-violet light with all other forms of light, we have a greater mixture of reagents.

That fact has a bearing upon this change of phosphorus, which is contrary to the change of sulphur, which is from the stable to the unstable form, and also the change of oxygen to ozone. It has been demonstrated that the light which comes to the earth from the sun contains light of those wave lengths when it reaches the ordinary part of the earth, which are inhabited, which decompose ozone, that is, changes the unstable to the stable form. Roscoe and others have shown that sunlight on elevations when the sun is at the zenith contains wave lengths of 300 μ, but not shorter ones. It has been shown by Regener and others that the effective ultra-violet waves which produce ozone from oxygen are shorter than 300 μ, approximately 257 μ, Perhaps phosphorus on exposure to ultra-violet light of suitable wave length may be observed to change in the same direction that sulphur and oxygen change.

The general proposition of the change from stable to unstable forms under the influence of ultra-violet light of short wave length has caused me to put forward a probable explanation of the formation of some of our chemical elements, which are unique in their conduct. I have been unable to find any reference to this explanation in the literature, so I am constrained to think it new.

The radio-active elements, accepting the term as applicable to those entities which have a definite combining value and characteristic spectrum, are supposed to break up or decompose at different rates or degrees. These complexities of elements, if we may so speak of them, are unstable and are changing to a stable form.

According to the hypothesis of Clarke and Laplace, worlds were produced by the cooling of highly heated nebulous forms of

matter which proceeds along certain lines of condensation to make various substances which we call elements. Perhaps under the influence of that initial form of energy, which we might just as well call light—even ultra-violet light—for if the temperature be sufficiently high the amount of ultra-violet light increases and the wave-lengths become shorter, some of the normal elements are changed from the stable to the unstable form like oxygen and sulphur are changed. It is barely possible, it is not beyond our imaginative conception, thus to account for the formation of the radio-active elements.

Mr. A. G. Betts (*communicated*): Dr. Bancroft has opened up practically a new subject of great possibilities, one of which may be the conversion of light energy direct to electricity. As silver chloride is decomposed by light, the electromotive force of a silver electrode coated with silver chloride in a chloride solution, ought to be different when illuminated, and when not. With two such electrodes alternately lit by sunlight, enough current should be produced to sound a telephone, for instance, with sufficiently rapid light alternation. I should like to know of some one's making a cell with a series of silver electrodes arranged as segments of a circle, above which revolves a slotted screen with openings the size and shape of the electrodes, and half as numerous, to produce alternating current direct from light. The silver electrodes would of course be connected up in two sets so that one set would be illuminated, while the other was not.

A paper read by title at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., April 30, 1908; President C. F. Burgess in the Chair.

ON THE NATURE OF ELECTROLYTIC CONDUCTORS.

By Louis Kahlenberg.

Ever since the discovery that water can be decomposed into hydrogen and oxygen by means of the electric current, the question as to the nature of the substances that suffer chemical decomposition when similarly placed in the path of a current of electricity has received careful experimental investigation. In this work the effort has naturally always been to ascertain what other peculiar chemical or physical properties electrolytic conductors have, besides the one of conducting the current with concomitant chemical decomposition, to which this latter power might be ascribed. The first systematic researches in this line were made by Michael Faraday, whose ingenious experiments are described in the volumes of his experimental researches. He showed that various fused salts and also solutions of different kinds may be electrolyzed, whereas other salts in the liquid state and other solutions are non-electrolytes. In connection with these experimental inquiries Faraday discovered his famous law, which lies at the basis of all electrolytic work; yet, though he gathered together a considerable number of facts as to what substances are electrolytic conductors and what substances are not, the question of the nature of electrolytes as contrasted with that of non-electrolytes really remained untouched. Later, Hittorf, in connection with his work on the differences in concentration that occur at the electrodes during the process of electrolysis voiced the opinion that electrolytes are salts, using the latter term in its broader sense, of course, so as to include acids and bases. Why many salts are non-electrolytes, and why electrolytes should have salt-like character, was, however, not explained.

Still later, Arrhenius made the claim that solutions showing greater diminution of the vapor tension, lowering of the freezing-

point and elevation of the boiling-point than they ought to according to the gas theory of solutions of van't Hoff, are electrolytes, and that in these solutions a peculiar decomposition of the dissolved substance into positively and negatively charged part-molecules takes place when solute and solvent are brought together. This latter assumption was required to make the behavior of many of the aqueous solutions of common saline substances harmonize with the gas theory of solutions, and it was soon claimed that since in solutions electrolytic conductivity is due to this peculiar electrolytic dissociation, the electrolytic conductivity, which many fused substances possess, must also be due to electrolytic dissociation. Now it is a well-known fact that many solutions, which do not show a greater lowering of the vapor tension, lowering of the freezing-point or elevation of the boiling-point than the gas theory requires, are yet most excellent electrolytes; and the same is true of many solutions which exhibit even a very much smaller lowering of the vapor tension, lowering of the freezing-point or elevation of the boiling-point than is required by the van't Hoff theory. Moreover, these statements hold for both aqueous and non-aqueous solutions. As an excellent example may be mentioned aqueous soap solutions, which boil at practically the same temperature as pure water and yet are excellent electrolytic conductors. As I have already in previous papers shown that the Arrhenius theory is inadequate and that it does not enable one to foretell whether a given substance will conduct electrolytically or not, it would be superfluous to enter upon further details concerning the matter here. The fact must calmly be faced that the vapor tension of solutions, and for that matter any other single physical property so far as we know, does not afford any basis whatsoever of a correct view as to the nature of electrolytes as contrasted with non-electrolytes. Nevertheless, the various views presented have all been useful in that they have stimulated experimental inquiry which has brought out a vast quantity of new facts, though the latter have in all cases shown that the views entertained as to the nature of electrolytic conductors are quite untenable, being founded upon by far too narrow a field of induction.

In any consideration of the conduction of electricity the great fact that the best conductors are metals ever looms up before us,

though, to be sure, the conductivity is in these cases not electrolytic in character. When the metals are combined with one another, alloys result, and these are also good conductors, though here too the composition of the alloy remains unchanged during the passage of the current. It is when the metal is combined with an element or elements of non-metallic character that the case becomes of prime interest in the present consideration, for the resulting combination may be an electrolyte or an insulator. Whether an electrolyte or a non-electrolyte results, depends upon the character of the metallic and non-metallic elements selected and the relative amounts of each entering into the combination. It need hardly be stated that the temperature is also a factor of consequence.

For example, take a metal of strongly pronounced metallic characteristics like tin and combine it with chlorine. We obtain at first stannous chloride and this is quite a good electrolyte when fused. If we chlorinate further, stannic chloride results and this is an insulator. This latter fact was also found by Faraday. Now, though stannic chloride is a non-conductor at ordinary temperatures, it might well be an electrolyte at lower or higher temperatures. This matter remained to be tested. I consequently heated the substance up slowly in a sealed tube containing a pair of platinum electrodes and tested the conductance of the substance from time to time. The heating was continued to the critical temperature of the liquid and higher, but the substance remained an insulator. Again, when the stannic chloride was gradually cooled from room temperature till it became a solid, it showed no power of conducting the current. Thus throughout the entire range of temperature from the solid state, through the melting point to the critical temperature and beyond, stannic chloride remained a non-electrolyte. Its non-electrolytic character was consequently not merely a question of state or of temperaure but rather one of composition. One can hardly escape the conviction that tin, which is a good metallic conductor, loses its power to conduct the current as the metal is united with chlorine, and that the conducting power is diminished more and more as more chlorine is added to the tin. In other words, by the addition of chlorine, which by itself is an insulator, the conductivity of tin is gradually drowned out. We continually state that when an element combines with another element a new compound is formed

with properties entirely different from those of the original elements with which we started. There is much truth in this; and yet it is also true that though each substance as it enters a chemical compound changes its properties more or less markedly, yet there is also a pronounced tendency to preserve its original properties after chemical union has occurred. In general, one may say that every element tends to preserve its properties as it enters a compound, so far as the other ingredients in the compound will permit it to do so. In such properties as mass, specific heat, refractive power and specific volume, which are known to be additive or approximately so, the elements exhibit in a large measure the properties in the combined state which they had in the free state. In the case of properties like the optical rotatory power and electrolytic conductivity which are not additive in character, the elements, or groups of elements, retain their original properties to a much less degree, though it would be quite incorrect to assert that they lose them entirely. In general we may say that in entering into chemical combination an element tends to retain its original properties as far as possible; that is to say, as far as the new conditions, under which it is placed in the compound, will permit. I shall not attempt to elaborate further upon this fact by citing specific instances. This would lead too far at present. Nor would it be necessary to dwell upon such special cases, for they are sufficiently well known to every chemist and physicist.

Now all metals have the power to conduct the electric current, to be sure, in varying degrees according to the nature of the metal. Furthermore, every metal as it enters a compound, tends to preserve its original power to conduct the current as far as possible under the new conditions in which it is placed in that compound. Nor need we use the word compound in its usual and narrow sense in this connection, for the statement holds also for those combinations which are commonly termed solutions. As above stated, when metals combine with one another, forming what are commonly termed alloys, the resulting product retains the power of conducting the current without manifesting decomposition. Changes of temperature, and consequently alterations of volume, of course, accompany the passage of the current through the alloys. When the metals are combined with non-metals there result insulators or electrolytes. In general it may be stated that

electrolytes are formed when metals are combined with a moderate amount of a pronounced non-metal. If the amount of the latter is unduly large, an insulator results, which we have seen exemplified in the case of the tetrachloride of tin. It is thus not at all strange that compounds containing metals should have conducting power, for the latter property would really be expected in the compound on account of the presence of the metal therein. Neither is it strange that in certain combinations of metals and non-metals, insulators are formed, for in these cases the amount and the effect of the non-metal may be so great as to completely overwhelm the tendency of the metal to conduct. In this, of course, not only the relative amount of the non-metal in the combination, but also its specific nature and the constitution of the compound enter in as determining factors, though, on the whole, the character of the non-metal and its relative amount seem to be of chief importance.

On the basis of the above considerations it would seem easy enough to see why some substances containing metals should be electrolytes and why others, which also contain metals, do not conduct. A great difficulty, however, arises in explaining why certain substances and solutions which contain no metals at all conduct electrolytically and others do not. In the face of the fact that in general compounds of metals with moderate amounts of non-metals form electrolytes, whereas there are also known compounds and notably solutions which conduct electrolytically and yet do not contain metals, one might well hold that the electrolytes which do not contain metals have yet a property which is characteristic of compounds containing metals. Consequently in this respect these electrolytes which are non-metallic in character, nevertheless exhibit a property which is characteristic of the majority of metallic compounds. In this category we have notably acids, and salts of non-metallic bases. The hydrogen of acids has always been considered by chemists as having metallic characteristics and the fact that liquid hydrogen has after all been found to be a non-conducting, colorless liquid, and solid hydrogen a colorless, transparent solid, has been somewhat disappointing to many chemists.

In so far as many non-metallic salts do possess the power to conduct electrolytically, they are akin to metallic salts. Indeed,

in consideration of the fact above mentioned, that metallic salts are very commonly electrolytes, one might almost incline to the view that, since the non-metallic electrolytic salts really have one of the very pronounced characteristics of metallic salts, namely—the power to conduct electricity, they represent a step toward the synthesis of the metals themselves.

It must not be overlooked that very many salts do not conduct electricity. So, for example, the chlorides of carbon, silicon, sulphur and titanium, the oleates, palmitates and stearates of the heavy metals, and in general all alkyl halides and esters of various kinds are insulators. And it must also be kept in mind that many compounds rich in content of heavy metal like zinc ethyl, mercury ethyl and other organic metallic compounds are yet non-conductors.

It is relatively easy to understand why the conductivity of a metal should be reduced by union with a non-metal commonly forming an electrolyte or an insulator; but it is not so easily comprehended why in certain cases the union of the two very poor conductors should result in a very good electrolyte. Cases where two or more good insulators unite to form a good conductor of the first class are not known. Cases where excellent first class conductors are transformed to either electrolytic conductors or insulators by chemical union with non-conductors are common; but we also have an abundance of cases where two insulators or at any rate very poor conductors yield a good electrolyte when combined with each other. As a typical example of the latter class, acetic acid and water may be cited. Both of these are very poor conductors indeed, whereas the combination of the two, the solution, conducts well. All efforts to explain such cases have thus far failed. These efforts, of course, have been directed toward finding some other physical or chemical property of the solvent or solute, or both, to which the peculiar electrolytic conductance of the resulting combination, the solution, could be ascribed. Thus the specific inductive capacity, the state of polymerization of the solvent have been invoked, but without avail, as I have shown repeatedly in my previous papers. The supposed relation between the so-called osmotic pressure, vapor tension or freezing and boiling points of solutions on the one hand and their electrolytic conductivity and chemical activity on the other has also repeatedly

been shown to be quite untenable. Moreover, the comparison of the so-called molecular conductivity of solutions at different dilutions really involves a comparison of conductors of different cross sections and so can not legitimately be used as a basis for further conclusions as to the nature of electrolytes, as is frequently done at present. The power of two non-conductors to unite to form a solution, or a compound in the narrower sense of the term, which is an electrolyte, is not confined to certain elements nor to certain peculiar combinations of elements. It must be admitted, of course, that all our notions as to the chemical constitution, so-called, of a compound are derived from the mode of building up or tearing down the compound and its behavior toward reagents. Our efforts to trace the power to conduct electrolytically to the chemical constitution of a compound are, therefore, simply efforts to find a relationship between electrolytic conductivity on the one hand and the behavior of the substance in question toward other chemical reagents on the other. And it is really not surprising at all that we should not be able to find any simple relationship to exist here. We do not know why a piece of silver conducts and a piece of sulphur does not, though the experimental fact in question has been known for a long time; and we are really much more in the dark as to why some compounds conduct electrolytically, others do not conduct at all, and still others conduct without decomposition. A frank acknowledgement of the actual situation seems to me very desirable, for it is bound to stimulate inquiry that will lead to a better comprehension of the phenomena of conduction. The few experiments which have been made thus far with induced currents in electrolytes show that when no electrodes are used electrolytes conduct the same as the metals themselves. The presence of electrodes seems consequently essential in order that electrolysis may take place.. The statement of Faraday that the electrodes are the doors at which the electrolytic products are eliminated by the electric current, which acts as an axis of force, is as adequate as ever in summing up the situation. The concentration changes which occur at the electrodes in solutions may be regarded as secondary phenomena produced by the chemical changes taking place at the surface of the plates. Experimental facts show that the viscosity is really quite a minor factor in determining the conductance of electrolytes. In the case of all

liquid electrolytes, Faraday's law has been found to hold at room temperatures and also at high temperatures. Recently tests in this laboratory have shown that it is also valid at quite low temperatures. In the cases of gases it is well known that Faraday's law generally does not hold. The study of radioactive phenomena and the power which various emanations have to make an air-gap conduct has rightfully aroused much interest, and experimentation and also speculation as to the nature of electricity and matter and their inter-relations. We must have very much more intelligent experimentation upon the subject of electrical conduction in general and electrolytic phenomena in particular before we can hope for a real improvement of our theories of the inter-relation of electricity and matter and our views of the process of electrolysis and the nature of electrolytic conductors.

University of Wisconsin,
April 27, 1908.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 2, 1908; President C. F. Burgess in the Chair.

DIRECT CURRENTS IN ELECTROLYTES WITHOUT ELECTRODES.

By Carl Hering.

In all the usual cases of electrolysis and electrolytic conduction, there are always two places in the complete electric circuit where the conductor changes from a metal, or conductor of the first class, to an electrolyte, or conductor of the second class, or vice versa. These transition points are the surfaces of contact of the liquid and the solid, namely, the active electrode surfaces. This must necessarily always be the case, because the sources of current are always metallic, or at least have metallic terminals. To make up a complete circuit of nothing but cells of different electrolytes, some of which will act as a current generator or battery, producing a current which circulates through the whole liquid circuit, appears to be impossible, as the energy reactions all add up to zero, just as in a complete circuit of thermoelectric couples at the same temperature, the sum of all the e. m. f's is always zero.

It has therefore been impossible, under the ordinary conditions, to divorce the electric or chemical actions at the electrodes from the actions in the electrolytes themselves, and our present knowledge therefore always involves both of these inseparably. Moreover, the supposed electrolytic migrations of the ions are, or may be, obscured or interfered with by the mechanical movements due to changes in specific gravities at the electrodes.

It has been maintained that some interesting and important knowledge might perhaps be gained if it were possible to produce such conditions that a direct current will flow through a complete circuit of electrolytes—that is, without any electrodes. The writer has long maintained that for many purposes the electrode action might be eliminated, in effect at least, by placing the

electrodes in relatively large end cells, at a relatively great distance from the part of the circuit under consideration and separated from it by one or more porous partitions, thereby preventing the changes of density, mechanical currents, chemical changes, and similar disturbing factors at the electrodes, from affecting the actions in the important part of the circuit under test. But it is maintained by some that even this is not entirely satisfactory, as the ions are supposed to receive their charges at and from the electrodes, and it must be conceded that the above-mentioned method of practically eliminating most of the actions at the electrodes does not eliminate this one. The largely accepted hypothesis of electrolysis is founded on this alleged transportation of charges from one electrode to the other. Hence, a question of interest naturally arises: What will happen if there are no electrodes to give the ions their charges? Will electrolytic conduction then become impossible and the electrolyte then become an insulator? Or, will it then conduct like a metal? If the latter, what will happen at the junctions of two different electrolytes, as, for instance, when they are separated by a porous partition? If the conduction is of the metallic kind, should not the usual chemical changes at the junctions then cease? Is it conceivable that such a change from one kind of conduction to the other, in one part of a circuit, will depend on whether the source of the current is at the possibly far-distant electrodes, or whether the current is generated in the liquid itself? If the electrodeless conduction is still of the electrolytic kind, where do the charges originate which the migrating ions carry? Could gases then be formed by electrolytic decomposition, and if so, where? Could anything at all, whether solid, liquid or gaseous, be set free if there are no electrodes? If so, would it not show the possibility of overcoming the electrode difficulties encountered in some forms of commercial electrolysis? Is the carrying of the charges by the ions the general and universal law, or is it only the law for the special (but usual) case in which electrodes are used? Is it a primary action, or is it merely a consequential one due to the use of electrodes?

These, and doubtless other questions of more or less interest, might perhaps be answered by experimenting with electrodeless

conduction. While the writer does not share the belief of some others, that there would be any radical or startling differences in a true case of electrodeless conduction, as compared with the case mentioned above, in which the effects of the electrodes have been virtually eliminated, yet he believes that the correctness of the important hypothesis of the carrying of charges might perhaps be tested by means of electrodeless conduction in which there is no source of such charges, and that controversies concerning the kind of conduction in electrolytes might perhaps be settled. Possible methods of obtaining electrodeless conduction may therefore be of interest, even though the results may not affect our present electrochemical operations; the object of the present paper is to suggest several methods.

The simplest way to produce a current in a complete circuit of electrolytes, without electrodes, would seem to be to induce it electro-magnetically, as is done in transformers. But, according to the law of such induction, as given by Maxwell and as usually stated in text books, it would be impossible to produce a prolonged direct current in a closed circuit in this way, because it is, of course, impossible to continue indefinitely to increase (or decrease) the magnetic flux enclosed by such a circuit; and according to that law as it is usually stated, it would be impossible to alternately increase and diminish this flux without producing an alternating current. Hence, we have in the past been led to believe that it is useless to try to do it in this way. A recent experiment made by the writer,* however, has shown that this law is in error if it is assumed to be a universal law, and that it *is* quite possible in one way, at least, and therefore possibly in others also, to increase or decrease the flux enclosed by a closed circuit without producing any induction whatsoever; it is therefore possible to induce a direct current in a closed circuit, even though this generally accepted law taught us that under those conditions only an alternating current would be obtained. We had for many years been misled by this law, which now turns out to be merely a special law applying only under certain specific conditions, and is not the universal or general one. Hence, the possibility is now opened

* "An Imperfection in the Usual Statement of the Fundamental Law of Electromagnetic Induction." Proceedings of the Amer. Inst. of Elec. Engrs., March, 1908, p. 339.

to us again to produce a direct current in a closed circuit by repeated induction with the same flux.

The above mentioned experiment in induction teaches us still another fact, which also makes new methods possible; it teaches us that there exists an important distinction between the conductor and the circuit. To produce induction, the conductor itself must cut across the flux; if the circuit alone does so, there will be no induction. This makes it possible to induce a direct current by repeated cutting of the same flux, namely, by cutting it in one direction with the conductor and in the reverse direction by the circuit only, the conductor remaining at rest, relatively, to the flux.

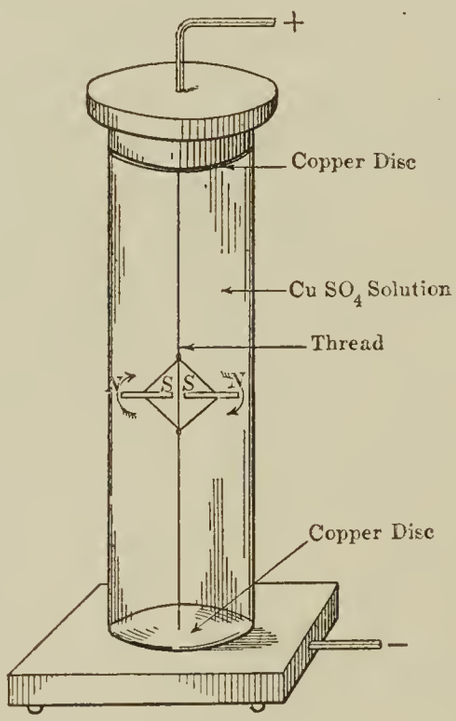

FIG. 1

There is another recent experiment which is also believed to be new, and although it was intended for an entirely different purpose, it also suggests a possible method of inducing currents in a complete electrolytic circuit. This very interesting, instructive and ingenious experiment was described by one of our members, Dr. E. F. Northrup,* to show the distribution of the magnetic flux in the inside of a conductor. The illustration is reproduced in the adjoining Fig. 1. Two bar magnets

* "Some Newly Observed Manifestations of Forces in the Interior of an Electric Conductor." By Edwin F. Northrup. Phys. Rev., Vol. XXIV, No. 6, June, 1907.

are mounted radially in a beaker containing an electrolyte, with like poles toward the central axis around which they are capable of rotating. If now a current is passed vertically through the electrolyte, these magnets will revolve, owing to the horizontal circular lines of flux in the electrolyte, due to the current. Incidentally, it might be added that it forms a radically new type of direct-current commutatorless motor.

This experiment suggested to the writer that according to Lenz's law, if such magnets are similarly revolved by external power, it must follow that a direct current will be induced in the electrolyte. All that is necessary, therefore, is to connect the top of the liquid with the bottom by means of a tube filled with an electrolyte, and the desired conditions for electrodeless conduction will be fulfilled. It will be readily understood that the magnets themselves do not form a necessary part of the conducting circuit; hence, they may be, and, in fact, had better be, insulated. Moreover, there may, of course, be several of these radial magnets, to increase the effect, and they may be replaced by a circular steel disk magnetized with one polarity at the circumference and the other at the center. Or they may be made electromagnets, either in the form of spokes or a flat iron disk, with a flat spiral coil fastened on one or both sides. Moreover, any desired number of flat magnets may be placed over each other on the same shaft with spaces for the liquid between them, thereby multiplying the e. m. f. proportionately; any desired e. m. f. could therefore be generated. In that case, however, provision must be made to keep the liquid between them from revolving with the magnets, as that would be fatal to the experiment, the theory requiring that the magnets move relatively to the liquid. This might be accomplished with stationary, flat, radial and insulated strips.

This method of inducing a current in an electrodeless circuit is correct in principle and will undoubtedly produce a direct current if the electrolyte will conduct, but it is somewhat wasteful, because electrical eddy currents will flow around the magnets and only a part of the current will flow through the outside tube or trough in which the actual tests and observations are to be made. This may not be a serious fault, provided the useful part of the current is sufficient, as the rest simply involves

the use of more power and the heating of the liquid, neither of which are serious in such an experiment. By using the following precautions, these losses of current may be greatly reduced. Disk magnets should be used, and they should fit the shaft and the inside wall of the vessel as closely as possible, so as to have as little liquid as possible around the edges of the magnets, as it is there that the eddy currents will flow; the perfect condition would be to have these joints liquid-proof. These disks must be perforated with some vertical holes or slots which connect the successive layers of liquid. The explanation of the induction in Fig. 1 seems to be that the flux radiates through the liquid from the center to the outer ends of the moving magnets, and this flux cuts the stationary liquid, producing a current in a vertical direction. When these magnets are made in the form of one solid horizontal disk revolving on its vertical axis, it seems to follow, from the statements of physicists, that this external flux will no longer revolve with the magnet, but will be stationary in space. In that case, the induction may be said to be in the liquid which is in the holes through the disk, as this then cuts the return flux which passes through the body of the magnet and which must then, of course, also be considered stationary in space. If the flux is conceived to revolve with the revolving disk, the explanation of the induction is like in the first case above, and the fact that there is then no counter induction in the holes is because the conducting liquid in the holes does not cut any flux, as it and the flux move together. The question of whether or not the flux revolves with the magnet is therefore not involved, as either will explain the result.

Another and probably better way to induce a current is to make the disk magnets like in Fig. 2, magnetized circularly and having a radial slot, thus producing a much stronger field between the two poles. When such a disk is revolved rapidly around its axis in an electrolyte, the liquid in the slot will flow outward radially, due to centrifugal force, thereby cutting the flux, and this will generate a current parallel to the axis. Each disk may have several slots, but this will not increase the e. m. f.; it will merely lower the internal resistance. But if there are several disks on the same shaft, one over the other, with a

space between, the e. m. f. will be increased proportionately. Here again there will be electrical eddy currents around the edges, unless the disk fits the vessel closely. The liquid between the disks must also be kept from revolving by means of stationary vanes.

Or the slot in the disk may be made spirally, as shown in Fig. 3, the disk being magnetized circularly, as before, so that

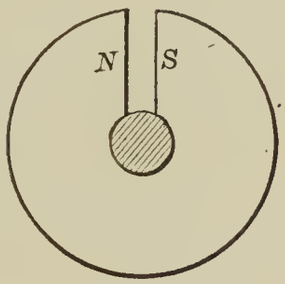

FIG. 2

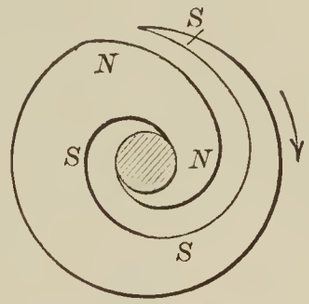

FIG. 3

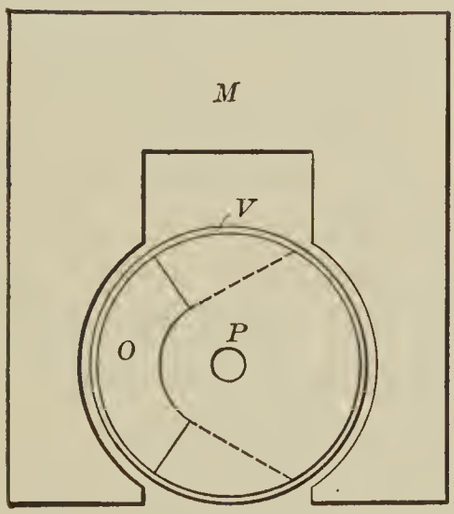

FIG. 4

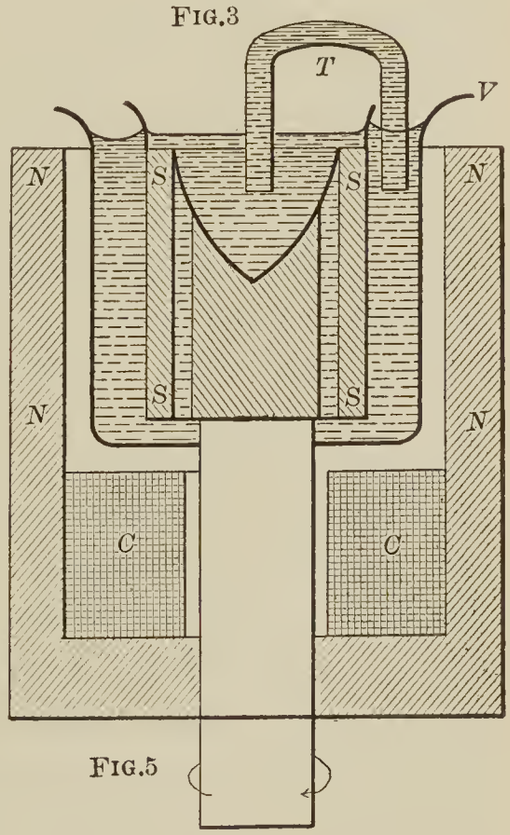

FIG. 5

one side of the slot is one pole and the other side is the other pole. It should be rotated in the direction shown. If the centrifugal force then is sufficient to prevent the liquid in the slot from being carried around with the magnet, that is, if the liquid in the slot moves only radially, an e. m. f. parallel to the axis will be produced, because the flux will then be cut by the liquid.

Another form is shown in Fig. 4. M is a magnet placed

horizontally; it may be an electromagnet, and therefore be very strong. V is a circular vertical vessel placed between its poles; it contains the liquid. P is a partition placed horizontally in this vessel, leaving only the opening, O; the edges of it around this hole should preferably be ground down to knife edges; this partition should be as thick as the polar surfaces are deep, vertically, and the magnet poles should preferably be relatively thin, vertically, so that this partition does not become too thick; it had better be made of insulating material and contain a piece of iron shown in dotted lines. There will then be an intense field produced in this hole, and nowhere else. If now the liquid be revolved around the axis of this vessel, say by vanes placed above and below this hole, an e. m. f. parallel to the axis will be produced. There may be several of these magnetic fields, increasing the e. m. f. proportionately.

Another possible form is shown in Fig. 5, which, like the previous form, has the advantage of low internal resistance and a strong electromagnet, but it is not possible to multiply the e. m. f., which will be that generated by a single cutting of only one field. The device is cylindrical and is shown in vertical cross-section. N N is one circular pole of an iron-clad magnet, with its exciting coil, C. The cylindrical block, S S, forms the other, or inside, pole and is revolved; it has longitudinal holes bored through it and preferably a cup-shaped depression in the top; it should preferably be insulated, depending upon the conditions. The vessel V, which may, though it need not, revolve, contains the liquid, but this liquid must be kept from revolving by vanes. The tube T, connecting the liquid in the middle with that in the annular space, is the outside circuit in which the tests are made; a horizontal open trough, connected at its two ends with the two liquid terminals of the generator, by means of tubes filled with the liquid, would be more convenient. It ought to be possible to generate between 1 and 2 volts in such an apparatus of moderate size and at not too high a speed. The induction will take place either in the annular space or else in the tubes, depending upon whether one considers the flux revolving or stationary in space.

Probably the simplest and most practical method, if a large magnet, such as those contained in most physical laboratories,

is at one's disposal, is to cause the electrolyte to flow vertically through a thin, flat tube of rectangular cross-section placed between the poles of the magnet; by making this tube quite thin and shaping it to fill and to fit the flat space between the two flat poles, a very intense field can be produced. An e. m. f. will then be generated and will tend to cause a current to flow in a horizontal direction across the flat column of liquid, perpendicularly to the flux and to the flow of liquid.

Referring to Fig. 6, which is a vertical cross-section of the tubes, and Fig. 7, which is a top view, a a is the vertical tube through which the liquid is caused to flow rapidly; it may flow downwardly from a tank above to one below; or better, it may be forced rapidly through this tube by a pump which takes the liquid from one end and forces it in at the other; this is admissible because there is no tendency for a current to flow lengthwise through this tube, and hence, the two ends may be connected and may make contact with a metal pump.

b b is the other tube, which may for convenience be an open trough; its two outer ends must meet, thus forming the complete circuit of the electrolyte used for experimenting. It must be electrically connected with the two sides of the vertical tube, and as the liquids in both must be separated mechanically, two porous partitions, p p, should be inserted, as shown. The current induced across the vertical tube will then circulate through the horizontal one. One pole of the magnet is directly behind the intersection of these two tubes and the other in front. If the polarity is as shown and if the liquid flows downward, the current will flow from right to left as shown. The liquid on the outsides of the porous partitions had better be the same as that which circulates, in order that no electrochemical changes take place at these two partitions to vitiate the results. With a very powerful electromagnet having tapered poles and a high velocity of the liquid, quite an appreciable e. m. f. could be produced, although at best it will be only a fraction of a volt. To increase the voltage, the vertical tube may be made to pass down and up through the field several times, as shown diagrammatically by the heavy black line in Fig. 8, which is a vertical section through the poles; the e. m. f. will then be multiplied proportionately. The

horizontal tube must then be connected as shown diagrammatically in Fig. 9, which is a top view; the electric currents in alternate passages of the moving liquid through the field will be in opposite directions, and hence, the neighboring edges must be electrically connected alternately as shown.

Dr. E. F. Northrup recently suggested the following as a possible method of generating a current in a circuit of electrolytes. If a complete circuit of electrolytes is made up of different electrolytes, at least two, separated by porous partitions, then if one of these junctions is heated and the other cooled, a current ought to circulate, if the thermoelectric e. m. f. between the liquids is sufficient. This has the advantage of extreme sim-

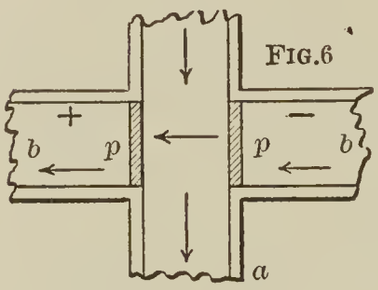

FIG.6

FIG.8

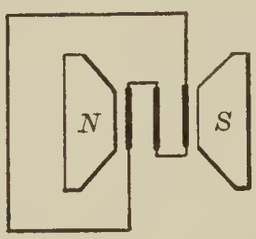

FIG.9

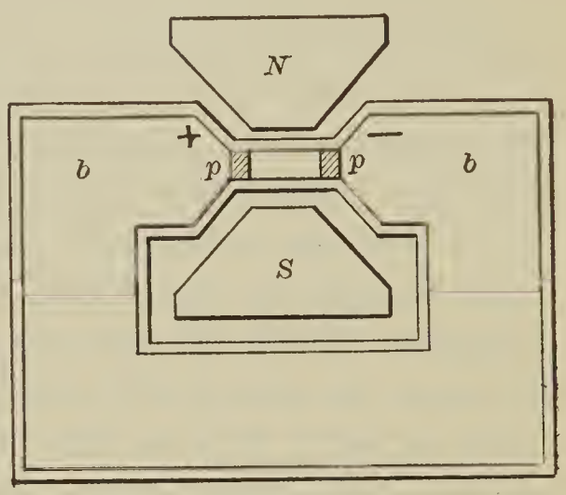

FIG.7

plicity, and the disadvantage of probably a very low e. m. f. and the introduction of the disturbing element of the heat, which will produce mechanical eddy currents in the liquid and may influence the chemical reactions, thereby interfering with the tests.

Still other methods were described or referred to in a paper, by the writer, on "Electrolytic Conduction without Electrodes," published in the Trans. Amer. Inst. Elec. Engrs., Vol XIX (1902), p. 309.

While most of these devices necessarily generate only a small e. m. f., lower than that required for many electrochemical reactions, yet that small e. m. f. will be sufficient to cause a chemical reaction to take place which may require a very much higher voltage if somewhere in the circuit a highly exothermic

reaction is made to take place. It seems to be a general principle that all the positive and negative energy reactions in a complete circuit of electrolytes add up to zero, from which it follows that even a slight additional e. m. f. would cause a current to flow, although a highly endothermic reaction is thereby caused to take place, as somewhere else in the circuit there will be an equally high exothermic reaction. This is illustrated in the case of two high voltage primary cells which have their two positive terminals connected together and their two negative terminals likewise connected, thus forming a complete circuit containing two equal and opposite e. m. f's. If now a slight e. m. f. is generated in one of these connecting wires, it may cause even a strong current to flow against the much higher e. m. f. of one of the cells; the energy for this will, of course, come chiefly from the other cell.

Moreover, a very weak current will suffice in a test with a complete electrolytic circuit to produce quite appreciable quantities of chemical changes, as the latter depends only on the coulombs, and not on the amperes; hence, by allowing the current to flow for a long while, easily measurable quantities of the products can be obtained with even extremely small currents. Although the resistance of that part of the circuit in which the induction takes place is necessarily high, in order not to weaken the magnetic field by a large air gap, there is no reason why the rest of the circuit containing the test cells should not have a large cross-section, and hence a low resistance.

It has been asked how it could be shown whether or not a current was flowing in such a circuit when there are no electrode reactions. When there is only one electrolyte, there might be difficulty in detecting a small current, although even in such a case a drop of potential method used in potentiometers could be used; the details of such a method applied to electrolytes were described by the writer in a paper on "Liquid Potentiometer; Determining Electrolytic Resistances with Direct Current Instruments," published in the Trans. Am. Inst. Elec. Eng., Vol. XIX (1902), p. 317. A simpler way would be to place in the circuit a cell containing a colored liquid, like sulphate of copper, and on each side of it, and separated by porous partitions, a cell containing a colorless liquid, like sulphuric acid; if the ions migrate through

the partition, as in ordinary electrolytic conduction, one or the other clear liquids will become colored, thereby also showing the direction of the current. If, as is claimed by some, the conduction without electrodes will be of the metallic order, then this change in color would not be produced, and the fall of potential method above mentioned, or some electromagnetic method, would have to be used.

The liquid used in that part of the circuit which comes into contact with metallic parts of machinery can be a neutral salt, like chloride of sodium, which does not react with the metal. While such metal parts should be insulated, this is not always essential, as the voltages in those parts of the circuit would generally be too low to cause the current to enter the metal and leave it again, unless the two reactions are reversible, and therefore together require no voltage of decomposition; the latter can readily be avoided.

The above-described possible methods of producing a direct current in an electrolyte without electrodes are offered here as mere suggestions, and not as descriptions of complete apparatus. Questions have been raised which, it seems, might perhaps be answered by such electrodeless conduction, notably the correctness of the generally accepted hypothesis of the carrying of charges and of the alleged metallic conduction of electrolytes; hence, the subject may be of interest, even though it be of no importance in the electrochemical industries.

Philadelphia, March, 1908.

DISCUSSION.

Mr. George Breed: Did Mr. Hering succeed in producing a momentary current in one direction by the influence of a magnetic field on a simple circuit consisting of an electrolyte only (say by the action of a magnet on a coil something like a bicycle tube filled with an electrolyte), which would influence a galvanometer needle?

Mr. Carl Hering: The paper gives no results of any tests,

but is merely a suggestion of methods for generating such currents. I have made no experiments, and therefore can give no results. Passing a current through a galvanometer would involve the introduction of electrodes, which would defeat the whole purpose, as there must, of course, be no metallic contacts in the circuit.

MR. BREED: Suppose you had a galvanometer constructed with a single coil, made up of the electrolyte itself in an insulated rubber tube, it would have about the same resistance as your fluid induction coil, into which you could introduce the magnetic lines. It seems to me you might possibly get a deflection without the use of metal electrodes at all.

PROF. W. D. BANCROFT: I hate to be positive about anything, of course, but my recollection is that some experiments were made by Kenrick[1] in Ostwald's laboratory, in which he put an electrode just above the surface of the liquid, and measured the potential difference. Under these circumstances, there was no electrode in contact with the electrolyte, but I think one could get electrolytic decomposition. If you believe that the conductivity of the electrolyte is metallic conductivity, or that an electrolyte is an insulator, it would be interesting to prove that. It does not seem to me conceivable, however, that the electrolytic action at the surface between two electrolytes can possible depend on the nature or existence of metallic electrodes which may be one hundred yards away. Consequently, I do not believe we shall get at that, even if we should succeed in realizing this gas experiment.

PROF. J. W. RICHARDS: One of our members, Prof. Hopkins, has shown that electrolytes do conduct, and I believe at one of our meetings he constructed a dynamo with an electrolyte as one of the circuits, and showed by the magnetic effect of the current of the circuit outside that it was conducting current.

PRESIDENT BURGESS: Mr. Marvin, in a paper before our Society a number of years ago, proved that an alternating current would pass through an electrolyte without electrodes.

PROF. RICHARDS: That experiment showed that an electrolyte in a tube acted in every respect as a conductor, but there is no experiment whatever that I have seen pointed out or brought

(1) Zeit. phys. Chem. **19**, 625 (1896).

forward which would show any essential difference in kind between the conduction of electricity through an electrolyte, in a continuous circuit, and a metallic circuit of the same ohmic resistance.

Mr. F. A. Lidbury: Do I understand that the resistance of a liquid electrolyte increases with the temperature when it is used as a secondary in the induction furnace, or something of that sort? Professor Richards said there was no difference in kind.

President Burgess: I doubt whether Mr. Richards meant that, as far as the temperature co-efficient is concerned, an electrolyte would have the same temperature co-efficient.

Mr. Lidbury: It acts the same way as regards resistance, as it would in an ordinary Kohlraush resistance cell.

Prof. Richards: There are metals or alloys whose temperature co-efficient is negligible or even negative, and there are electrolytes whose temperature co-efficient is negligible or even positive, so that no difference *in kind* can be predicated between these conductors in this respect.

Mr. F. A. Lidbury *(communicated)*: I really cannot see what is to be gained by attempting to draw comparisons where they do not exist such as Dr. Richards does in stating that conducting electrodeless solutions would conduct "metallically." It seems to me, on the other hand, that comparisons of this sort are liable to lead to much confusion of thought. As Dr. Bancroft has emphasized, it is not obvious how the presence or absence of electrodes at the ends of a system could possibly affect the nature of the conduction in the body of the electrolyte or chain of electrolytes as the case may be. If one thing is more certain than another in respect to electrodeless conduction in the case of any given electrolyte or chain of electrolytes, it is that the phenomena associated with the passage of electricity through the electrolyte itself must be the same both quantitatively and qualitatively whether the passage of that current is brought about by or without the aid of electrodes. Thus the resistivity and the temperature co-efficient of resistivity must be the same in both cases; the same phenomena must occur at the boundary points of the various solutions in a chain of different electrolytic solutions; in short, as far as the laws governing the passage of electricity

through an electrolyte is concerned, it is utterly immaterial whether electrodes are used or not.

MR. CARL HERING *(communicated)*: Mr. Breed's suggestion to make a galvanometer coil of a rubber tube containing the electrolyte has been suggested before; this would merely serve to detect the existence of a current which I think can be easily done in other ways; the difficulty is to generate the current and not to detect it. Replying to Dr. Bancroft and Mr. Lidbury, I desire to say that I distinctly disclaimed in the paper any partiality toward the suggestion that electrolytes conduct metallically or act as an insulator; I merely explained the suggestions made by others. My only opinion is expressed in the paper itself to the effect that I did not believe that there would be any radical or startling differences in a true case of electrodeless conduction, as compared with the case mentioned in the paper in which the effects of the electrodes have been virtually eliminated, and therefore I agree with the closing remarks of Mr. Lidbury. I presume the question of whether an electrolyte under those circumstances will conduct at all has been settled in the affirmative by experiments with alternating currents, hence the main question is, what is the nature of the conduction, that is whether it is different or like the conduction in metals. The question of temperature co-efficient has nothing to do with it, as there are solids like carbon whose temperature co-efficient is negative, and Prof. Richards says there are electrolytes whose temperature co-efficient is positive. I agree with Mr. Lidbury that quantitatively and qualitatively the passage of electricity through an electrolyte would be independent of whether there are electrodes or not, provided the word "qualitatively" does not include the nature of the conduction, which at present is believed by many to be typically different in electrolytes than in metals. It might be of interest to use as electrolytes two of the ionized air resistance described by Mr. Bronson at this meeting, holding them above the liquid, but this would not be true electrodeless conduction in the sense in which I used the term in this paper: it would merely be using electrodes of conducting air in place of metallic electrodes, and the question would then arise, does this air conduct like a metal or by the carrying of charges by the ions as is assumed to be the case in electrolytes? In either case there would still be present metallic electrodes.

A paper read by Dr. W. D. Bancroft at the Thirteenth General Meeting of the Electrochemical Society, at Albany, N. Y., May 2, 1908; President C. F. Burgess in the Chair.

REVERSED ELECTROLYSIS.

By J. W. Turrentine.

"In the case of electrolysis the only specific action which we have to attribute to the current is that it tends to set free the anions at the anode and the cations at the cathode."[1] At the anode this action may result in the formation of new cations due to the corrosion of the anode by the liberated anions. Employing a different terminology, these facts may be expressed as the diminution of electric charges on the cations at the cathode and the increase of like charges at the anode. The electric charges of an ion may be looked upon as the manifestation of valence if we regard valence as potential combining capacity. If we define oxidation or reduction as a change in valence and keep in mind the theory of valence changes, from either viewpoint it is seen that at the cathode we have a reduction and at the anode, an oxidation. So, we may adopt as a rule that electrolysis in aqueous solution invariably leads to oxidation at the anode and reduction at the cathode.

Oxidation at the anode may be fully explained by the simple chemical action of the discharged anion, and reduction at the cathode by the action, likewise, of the discharged cation. Anions being electronegative in character, on being discharged at the anode, they appear as strong oxidizing substances and either escape as such or corrode the anode or react with some oxidizable substance in the electrolytic bath. In an analogous manner may be explained the corresponding reduction at the cathode.

In pure chemistry we understand oxidation as meaning the addition of electronegative substances, as oxygen, or the subtraction of electropositive substances, as hydrogen, and a reduction as the reverse. Since either process may manifest itself as

[1] Bancroft. Trans. Am. Electrochem. Soc., 8, 33 (1905).

a change in valence or the number of electric changes of the ion acted upon, the chemical and electrochemical oxidation—reduction phenomena are practically identical.

The reduction of one substance results in the oxidation of the reducing agent—which fact is as well known as the law of the conservation of energy. The products of a reduction, however, may appear to be more potent reducing agents than the agent which induced the reaction leading to their formation. A parallel statement may be made in regard to the products of the oxidation of hydrozine by numerous oxidizing agents,[2] yet the ratio of hydrogen to nitrogen is higher in ammonia than that in hydrozine, but the former is a weaker reducing agent than the latter on account of its greater stability. Likewise, the oxidation of phosphine by oxygen,[3] when the two gases, highly diluted by some neutral gas, are allowed to mix slowly by diffusion, results in the production of free hydrogen, according to the equation

$$2HP_3 + 2O_2 = 2HPO_2 + 2H_2$$

yielding a product more highly reduced than the reducing agent itself, though, as in the previous case, more stable than the reducing agent.

Potassium permanganate and hydrogen peroxide act towards each other in acid solution as mutual reducing agents, each giving up a part of its oxygen.[4]

Depending on conditions, hydrogen peroxide may act both as an oxidizing and as a reducing agent, in either case giving up one-half of its oxygen.

Such irregularities may be explained on the basis of an intermediate reaction, though the existence of such a reaction cannot always be demonstrated. Secondary reactions may take place which effectively conceal the primary reaction so that the ultimate result may appear as a reduction by an oxidizing agent or an oxidation by a reducing agent.

In the electrolysis of aqueous solutions a reversal of the usual order of things to which we have given the designation of reversed electrolysis, must always be considered as the result of secondary reactions since, from definition, the primary reaction

[2] Browne and Shetterly, Jour. Am. Chem. Soc., **29**, 1305 (1907); **30**, 53 (1908).
[3] Van der Stadt, Zeit. phys. Chem., **12**, 322 (1893).
[4] Brodie, Jour. Chem. Soc., **7**, 304 (1855); Lunge, Zeit. angew. Chem. (1890), p. 6.

is always one of oxidation at the anode and of reduction at the cathode. Such cases are numerous. Luther[5] shows that when Fehling's solution is electrolyzed, cuprous oxide is deposited on the anode as well as metallic copper on the cathode, a reduction resulting at both poles. The direct and primary action of the current is the oxidation of the tartaric acid to formic acid, an oxidation product but a less stable substance which reduces the cupric salt and precipitates on the anode cuprous oxide. In the same way gold can also be reduced and deposited, as also, in methyl alcohol solution, if alkaline, when aldehyde is produced at the anode.

In an ammoniacal solution of potassium bromide, potassium permanganate is reduced to the green manganate at the anode. This result is brought about through the oxidation of bromide at the anode to hypobromite; this oxidizes the ammonium hydroxide to hydroxylamine which in turn reduces the permanganate, purple, to the manganate, green. Also, when a gold salt, or a permanganate, is present in a saturated solution of an alkaline carbonate, upon electrolysis, reduction occurs at the anode due to the formation there of percarbonates which, breaking down in the aqueous solution, yield as a product hydrogen peroxide. This acts as the reducing agent toward the gold and the permanganate.

Yet more striking is the reversal obtained when a dilute solution of nitric acid containing potassium iodine is electrolyzed—iodine being liberated at the cathode as well as at the anode. Nitric acid on electrolysis is reduced to nitrous acid. The latter reacts at once with potassium iodine, oxidizing it and liberating iodine against the cathode.

Tommasi,[6] on electrolyzing a solution of chloral hydrate obtained chlorine at the cathode. Wood and Jones[7] obtained a deposit of metalic copper simultaneously at both poles from a solution of the double carbonate of copper and potassium. This we may explain as we did the deposition of gold from the carbonate solution as due to a reduction by hydrogen peroxide which had been produced by the decompositions of percarbonates.

Kraus,[8] in his interesting work on solutions of metals in

[5] Zeit. Electrochem, 8, 645 (1902).
[6] Elektrochemie, 741.
[7] Proc. Cam. Phil. Soc., 14, II, 171 (1907).
[8] Jour. Am. Chem. Soc., 29, 1556 (1907).

liquid ammonia, furnishes us with the most perfect instance of reversed electrolysis, though hardly comparable to the other cases cited as it does not have to do with aqueous solutions. When a solution of sodium in liquid ammonia is electrolyzed between lead electrodes lead is dissolved from the *cathode* and appears in the solution as negatively charged ions of Pb_2. The observed loss in weight of the cathode agrees almost perfectly with the value calculated from the electro-chemical equivalent of lead.

HYDROGEN AT THE ANODE.

Beetz[9] has described experiments in which he obtained an evolution of hydrogen from the anode when he electrolyzed a solution of magnesium sulphate between magnesium electrodes. Thin magnesium wire electrodes of the size of knitting needles were projected through the bottom of a glass vessel. The anode, he noted, became covered by a black substance, supposed by the author to be a suboxide of magnesium, which slowly dissolved with an evolution of hydrogen and which, also, filled the solutions in the anode region, causing turbidity. As these phenomena would indicate a disintegration of the anode with subsequent decomposition of water by the finely divided magnesium (as the author himself deemed possible), a similar experiment was performed in connection with this paper, as follows:

A solution of sodium sulphate (5 gr. to 250 cc H_2O) was electrolyzed between a platinum cathode and a magnesium anode. The anode consisted of a bunch of magnesium ribbon sealed in the end of a glass tube by means of cerusine. The tube was bent back upon itself so that the anode in its end could be thrust into an inverted burette which served as eudiometer. An "oxy-hydrogen gas" coulometer was joined in series. The accumulated gas was withdrawn and analyzed over alkaline pyrogallol in a Hempel pipette. The residue, after being subjected to qualitative tests, was taken as hydrogen. Under the conditions of the experiment the current density at the anode could not be estimated nor maintained constant, so the different measurements obtained can hardly be compared with each other. It is seen from Table

[9] Phil. Mag., 32, 269 (1866); Pogg. Ann., 127, 45. Cf. also Elsässer, Ber. 9, 1818 (1876); 11, 587 (1878).

I that the evolution of gas from the anode was vigorous and, from the analysis, was almost pure hydrogen.

TABLE I.

Gases from Magnesium Anode.				Gases from Coulometer.		
No.	Total.	O_2	H_2	T.V.	O_2	H_2
	c.c.	c.c.	c.c.	c.c	c.c.	c.c.
1	31.2	1.0	30.2	——	——	——
2	18.8	0.6	18.2	28.2	9 4	18.8
3	13.8	0.6	13.2	26.3	8.7	17.6
4	9.4	0 8	8.6	30.5	10.2	20.3
5	12.7	0.6	12.1	40.0	13.3	26.7
6	14.4	0.4	14.0	40.5	13.5	27.0
7	4.8	0.2	4 6	15.0	5 0	10.0

While the results shown in this table verified Beeetz's observation as to the evolution of hydrogen, no indication was obtained of the formation of a black compound or of the disintegration of the anode. The corrosion of the anode was in every case rapid and led to the appearance of a voluminous white precipitate of magnesium hydroxide in the anode region. Bubbles of gas occasionally came off from the precipitate, but seemed to be merely the escape of the entangled hydrogen. The magnesium anode remained white and became covered with scales of magnesium hydroxide, periodically dislodged by the vigorous evolution of gas. On breaking the current the cessation of the evolution was not sharp, which fact would indicate the formation of some compound which gradually decomposed water. Such a substance could only be metallic magnesium or a compound of magnesium in which the effective valence of the magnesium is less than two. If the latter it would be acting analogously to cuprous sulphate which, in cold solutions, breaks down and deposits metallic copper, and to chromous salts, which react with water and evolve hydrogen.[10]

The absence of a visible change in the surface of the anode and yet a free evolution of hydrogen, persisting for a short time after the curent had been broken would make it appear that this decomposition of water is quite analogous to that of chromous

[10] Ufer, Liebig's Ann., 112, 302 (1859).

salts. Instead of the product of the electrolysis appearing as a solid, as noted by Beetz, these experiments would rather indicate the actual solution of the anode as *magnesious* sulphate which at once reacted with the water of the electrolytic bath and formed magnesic sulphate and hydroxide, according to the equation

$$Mg_2SO_4 + 2H_2O = MgSO_4 + Mg\ (OH)_2 + H_2.$$

This reaction would account for the evolution of hydrogen and for the voluminous precipitate of magnesium hydroxide in the immediate region of the anode. The scale of magnesium hydroxide surrounding the anode, by allowing slow diffusion outward of the instable salt, would afford an explanation of the continuation of the evolution of hydrogen after the interruption of the electrolysis.

Beetz made a series of quantitative measurements of the hydrogen evolved from the poles and of the magnesium dissolved from the positive pole. In every case he found that the combined volumes of the gas evolved from the two electrodes was approximately equivalent to the weight of the magnesium dissolved from the anode.

These measurements are not inconsistent with our assumption of the ocurrence under these conditions of Mg with a lower valence, but they can not, from the nature of the case, prove the existence of such a form. Indeed, in the example mentioned above of the oxidation by water of an instable compound, in which the metal is apparently oxidized from a lower to a higher valence, we may be dealing solely with a question of linkage of molecules and not with one of a change of valence. Mercurous nitrate, we know from the work of Ogg[11] must be considered as $HgNO_3$. $HgNO_3$. If written $\begin{matrix} Hg - NO_3 \\ Hg - NO_3 \end{matrix}$, an actual difference in valence between the mercury in this molecule and that of the mercury in $Hg \begin{matrix} - NO_3 \\ - NO_3 \end{matrix}$ does not exist.

To bring the structural formula for ferric chloride into agreement with certain of its reactions it must be considered as $Fe_2\ Cl_6$.

[11] Zeit. phys. Chem., 27, 285 (1898).

Chromous sulphate may then be $\begin{matrix} Cr - SO_4 \\ | \\ Cr - SO_4 \end{matrix}$; magnesium sulphate may be $\begin{matrix} Mg \\ Mg \end{matrix} > SO_4$ or $SO_4 < \begin{matrix} Mg - Mg \\ Mg - Mg \end{matrix} > SO_4$.

But the matter of linkage is entirely aside from the question of valence as considered from the electrochemical standpoint. Linkage may exist. There may be no actual change in the valence of a metal. But there is an effective valence, based on Faraday's law and the electrochemical equivalents, and which manifests itself in every electrolytic corrosion. It is with the effective valence that we have to do in this paper.

This belief in the lower valence of magnesium is substantiated by the works of others. Christomanos[12] obtained a gray powder when he suddenly cooled a magnesium flame which, from its analysis, appears to have the formula Mg_8O_5, but which he regarded as a mixture of magnesium and magnesium oxide. Baborovsky[13] considers the suboxide obtained by Christomanos identical with that noted by Beetz. Considerable light could be thrown on this point if the compound prepared by Christomanos were placed in water; an evolution of hydrogen would strongly indicate the correctness of Baborovsky's contention.

White,[14] in his study of the action of solutions of bleaching powder on metals, observed that magnesium and aluminum are distinctive in that, while other metals studied, as iron, copper, nickel, etc., evolved oxygen, these two evolved hydrogen, the magnesium producing as much as 500 cc in twelve hours.

Luther and Schilow[15] employ the hypothetical magnesium of a valence of one to explain the reaction which takes place between iodine, methyl alcohol and magnesium,[16] in which hydrogen is evolved. Their supposition of an intermediate reaction in which is formed a *magnesious* iodide is represented by the equations

$$Mg + \tfrac{1}{2} I_2 = Mg\ I$$
$$Mg\ I + CH_3OH = Mg\ IOCH_3 + \tfrac{1}{2}\ H_2.$$

[12] Ber. chem. Ges., Berlin, **36**, 2076 (1903).

[13] Ber. chem. Ges., Berlin, **36**, 2719 (1903).

[14] Jour. Soc. Chem. Ind., **22**, 132 (1903).

[15] Zeit. phys. Chem., **46**, 803 (1903).

[16] "Data on the Chemical Role of Catalytic Agents," Jour Russ. phys. Chem. Gesell, **35**, 309; Chem. Centrlb., **711**, 277 (1903).

In short, while the evidence adduced above does not establish the existence of monovalent magnesium, yet the chemistry and the electrochemistry of the metal demand the assumption of such a form.

HYDROGEN AT AN ALUMINUM ANODE.

In the chlorination of organic compounds where the so-called "carriers" are employed, aluminum chloride, ferric chloride and stannic chloride, all behave practically identically. Ferric chloride and stannic chloride are both susceptible of a reduction to a lower chloride, thus furnishing an explanation of their role as catalytic agents in chlorination processes on the ground of intermediate reactions in which the ferric or stannic compound, in conveying chlorine into the molecule of the body to be chlorinated, is reduced to the ferrous or stannous compound, respectively, and is subsequently reoxidized, the oxidation taking place instantaneously. The close analogy between aluminum and iron and tin as carriers of chlorine made it seem aluminum and iron analogy extended to the matter of valence, our lack of knowledge of aluminum compounds, in which the aluminum appears with a valence other than three, being absolute because of the great instability of such compounds. The position of aluminum in the periodic system, furthermore, being a close neighbor of both carbon and boron, makes it appear odd that this element does not exhibit the property of linkage as do both carbon and boron. The evidence obtained as to the dual nature of magnesium from the behavior of that metal when made anode led to the belief that a clue could also be gotten in the same way to the existence of aluminum with an effective valence lower than three. Accordingly, actuated by these considerations alone, we made aluminum anode in a solution of sodium chloride containing 10 gr. of the salt to 200 cc distilled water. The same apparatus was employed here as that used in the like experiment with the magnesium anode.

A strip of aluminum foil was sealed, by means of cerusine, in a glass tube so bent that the exposed end of the foil, which was to serve as anode, could be projected into the mouth of an inverted burette to serve as eudiometer. Each face of the anode was about a square centimeter in dimensions. For cathode was

employed a strip of platinum foil. A gas coulometer was joined in series with the electrolytic cell. The accumulated gases were withdrawn from the eudimeter into a Hempel gas burette, were measured and were then analyzed for oxygen by shaking with alkaline pyrogallol in a Hempel pipette. The residual volume, which gave affirmative qualitative tests, was taken as hydrogen. The results are given in Table II.

TABLE II.

Gases from Aluminum Anode.				Gases from Coulometer.		
No.	Total.	O_2	H_2	T.V.	O_2	H_2
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
1	5.0	0.2	4.8	40.0	13.3	26.6
2	5.4	0.2	5.2	50.0	16.6	33.4
3	5.8	0.1	5.7	45.0	15.0	30.0
4	10.6	0.1	10.5			

The anode was rapidly corroded as a high current density was used; and, as in the case of the magnesium, the solution became clouded with a voluminous precipitate of aluminum hydroxide of the characteristic gelatinous consistency. The evolution of hydrogen persisted for a few minutes after the electrolysis had been discontinued.

Unfortunately, electrochemical methods and efficiency measurements do not admit of the determination of the effective valence at which a metal is dissolving from the anode when the entire corrosion does not take place in accordance with that figure. When the metal has the choice of a number of possible valencies still greater are one's difficulties. This is readily seen from an illustration. If the aluminum dissolved quantitatively on the trivalent basis, stable aluminum trichloride would be formed and no hydrogen evolved. If it dissolved quantitatively to aluminum dichloride, the reaction with water could be represented thus:

$$6AlCl_2 + 6H_2O = 4ACl_3 + 2Al(OH)_3 + 3H_2;$$

if to the monochloride, the equation

$$6AlCl + 6H_2O = 2AlCl_3 + 4Al(OH)_3 + 3H_2;$$

would represent its reaction in water. On the above basis from the ratio of the aluminum chloride in solution or of the precipitated $Al(OH)_3$ to the hydrogen evolved could be determined readily enough whether the aluminum dissolved as the monovalent or as the divalent form. However, it is impossible to show from such analytical data, when we are not hypothesizing a quantitative corrosion as one definite electrochemical equivalent, that the corrosion has not taken place at any one of the numerous possible percentage combinations of the three valencies.

If, however, the yield of hydrogen at the anode could be shown to increase with increasing current density and could be made to approach asymptotically a certain definite value, a clue could be obtained as to the form of aluminum with which we are dealing which is not based on analogy and supposition.

The striking similarity of behavior between the magnesium and the aluminum is further instanced by the like behavior of the two in bleaching powder solution,[17] where they both dissolve with the evolution of hydrogen.

Wöhler and Buff, in an article entitled "A Compound of Silicon with Hydrogen," published some fifty years ago[18] made note of the evolution of hydrogen at an aluminum anode. The subject has since been discussed by Norden [19] who produces evidence also from mineralogical and other sources to substantiate the hypothesis of the probable existence of aluminum of a lower valence.

OXYGEN AT THE CATHODE.

The statement of Victor Meyer[20] that hydrogen, if shaken with a solution of potassium permanganate, is absorbed and that an equivalent (one-half the volume) amount of oxygen is evolved led to the belief that such a reduction with accompanying secondary reactions could be duplicated electrolytically. Accordingly, a solution of potassium permanganate, containing 5% by weight of $KMNO_4$ and 2.5% by volume of concentrated sulphuric acid, was electrolyzed between platinum electrodes in a specially constructed cell. The cell consisted of a beaker of

[17] White, loc. cit.
[18] Liebig's Ann., **103**, 218 (1857).
[19] Zeit. Elektrochemie, **6**, 159 (1899-1900).
[20] Meyer and Recklinghausen, Ber, Chem. Ges., Berlin, **29**, 2549 (1896).

200 cc capacity in which, to serve as cathode compartment, was inverted a 100 cc graduated tube, drawn out at its upper end into a capillary tube and closed with rubber tubing and screw clamp. The platinum plate to serve as cathode, about 3 cm^2 on a face, was fastened to a short wire which was fused in the end of a narrow glass tube; the tube was so bent that the cathode could be projected up into the inverted, graduated tube. Connection was made with the cathode by filling the narrow tube in which it was sealed, with mercury. To prevent the diffusion of the anode gases into the cathode compartment, the anode was carefully enclosed in a parchment envelope. Connection was then completed through a Rühstrat resistance frame and milammeter, with the storage cells. The solution was placed in the cell and drawn up into the eudiometer until it had displaced the air therein; a current was then passed until a convenient volume of gas had been collected in the eudiometer, upon which it was withdrawn into a gas burette, was measured and was analyzed for oxygen by shaking with alkaline pyrogallol in a Hempel pipette. The residue from the absorption after being subjected to qualitative tests, was in each case taken as hydrogen.

There was obtained in every case, as shown by Table III. a marked evolution of oxygen from the cathode:

TABLE III.

	Cathode Gases.				
No.	Total.	H_2	O_2	Milliamps.	Time.
	c.c.	c.c.	c.c.		Hours.
1	42.0	29.9	12.1	125.	1.75
2	25.6	17.9	7.7	65.	1.5
3	26.6	19 0	7.6	25.	5.0
4	52.0	43.5	8.5	250.	1.0
5	50.6	42.0	8.6	1.	18.0
6	10.8	5.0	5.8	50.	1.5
7	12.7	7.0	5.7	50.	1.2

The cathode became heavily encrusted with a hard and compact coating of manganese dioxide which cracked and fell off, only to be reformed. The solution, also, became thick with a

black precipitate which, without analysis, was taken to be manganese dioxide.

Morse,[21] replying[22] to the paper of Meyer,[23] showed that a spontaneous decomposition of potassium permanganate occurs in solutions of this compound[24] in the presence of manganese dioxide, with an evolution of oxygen and that the reaction involved is accelerated by an increase in the amount of manganese dioxide present. With this fact in mind a number of blank experiments were run with solutions of the same concentration as above and contained in the same apparatus as that in which the electrolysis was conducted. As it was observed that the spontaneous evolution of oxygen increased up to certain limits with the age of the solution, due, no doubt, as stated by Morse, to the accumulated manganese dioxide in the solution, the blank experiments were run both before and after the experiments in which electrolysis was employed. On the basis of the average rate of evolution of oxygen thus procured were made corrections in the calculations which followed. In Table IV. may be seen the results of a number of the blank experiments:

TABLE IV.

No.	Time.	O_2	No.	Time.	O_2	No.	Time.	O_2
	Hours.	c.c.		Hours.	c.c.		Hours.	c.c.
1	10	8.0	4	12	2.5	7	36	13.
2	12	9.0	5	48	34.0	8	24	10.
3	24	18.0	6	36	21.0	9	42	27.

If corrections are applied to the values shown in Table 3, on the basis of the figures in Table IV. it is evident that the evolution of hydrogen at the cathode has been greatly accelerated by the electrolysis.

When a solution similar to that used in the above experiments was electrolyzed in a single-arm gas coulometer, the anode and cathode gases being caught together, the following figures were obtained:

[21] Morse, Hopkins and Walker, Am. Chem. Jour., **18**, 401 (1896).
[22] Ber. chem. Ges., Berlin, **30**, 48 (1897).
[23] Loc. cit.
[24] Cf. Thenard, Comptes rendus, **42**, 382 (1856).

TABLE V.

No.	Total.	H_2	O_2	No.	T.V.	H_2	O_2
	c.c.	c.c.	c.c.		c.c.	c.c.	c.c.
1	15.6	1.0	14.6	5	12.8	1.5	11.3
2	4.4	1.4	3 0	6	17.6	1.2	16.4
3	10 0	1.0	9.0	7	17.4	1.5	15.9
4	5.8	0.3	5.5	8	17.2	1.0	16.0

which show that the yield of hydrogen was practically nil, or, as shown by Meyer, and also by Jones,[25] which seems more probable, that the hydrogen was absorbed by the permanganate. Yet more probable does it appear that the reduction in the evolution of hydrogen from the cathode is a matter explainable by the proximity of the anode to the cathode, the oxygen there evolved acting possibly as a depolarizer at the cathode.

To determine the cathode efficiency in hydrogen and oxygen so that a ratio could be obtained between the oxygen evolved at the cathode and the hydrogen which failed to be evolved, an "oxy-hydrogen gas" coulometer, filled with dilute sulphuric acid, was placed in the circuit in series with the electrolytic cell. A number of these results, chosen at random from a large number obtained, are given in Table VI.

The ratios, however, obtained on the above basis, varied widely; the results could not be duplicated even though all the conditions within one's control were maintained constant.

In attempting to explain the anomaly of the evolution of oxygen from the cathode the hypothesis of a secondary reaction, from analogy within such cases, was adopted. And in the remaining pages will be given, as briefly as possible, a description of the experiments performed with the views which lead to their performance, in our attempts to arrive at an understanding of the underlying chemistry of the electrolytic reductions of potassium permanganate. Morse[26] explained the catalytic action of manganese dioxide on potassium permanganate on the ground that the former behaves as a carrier of oxygen. In substantiation, he showed by analysis that manganese dioxide, on standing

[25] Jour. Chem. Soc., 33, 95 (1878).
[26] Loc. cit.

in air lost oxygen and on being replaced in a solution of potassium permanganate regained oxygen. To use this fact as an explanation of our observations, the acceleration of the cathode reaction by the current must be due to the formation of a particularly reactive form of manganese dioxide, MnO_2, which was oxidized by the Mn_2O_7 to a higher, instable oxide, as Mn_2O_5, this at once breaking down with the evolution of oxygen. Such a reactive form of MnO_2 might be a soluble form of tetravalent

TABLE VI.

Cathode Gases from $HMnO_4$				Gases from Coulometer.			Ratio of Oxygen Evolved to Hydrogen Absorbed. (On basis $O_2=2H_2$) Approximate.	
No.	Total.	H_2	O_2	Total.	H_2	O_2		
1	15.0	10.0	5.0	75.0	50.0	25.0	10:40	1:4
2	16.2	10 4	5.8	40.0	26.7	13.3	12:16	3:4
3	22 6	15.6	7.0	42.0	28.0	14 0	14:13	1:1
4	23.2	16.7	6.5	40.0	26.7	13.3	13:10	1:1
5	24.2	19.2	5.0	60.0	40.0	20.0	10:21	1:2
6	9.6	8.1	1.5	41.0	27.3	13 7	3:19	1:6
7	16.8	13.2	3.6	50.0	33.4	16.6	7:10	2:3
8	17.8	14.6	3.2	39.0	26 0	13.0	6:12	1:2
9	20.4	17.2	3.2	41.0	27.3	13.8	6:10	1:2
10	15.8	14.0	1.8	28.0	18.7	9.3	4:5	4:5
11	14 0	10.0	4.0	35.6	23.8	11.8	8:14	4:7
12	24.2	20.3	3.9	45.0	30.0	15.0	8:10	4:5
13	18.3	14.2	4.1	40.0	26.7	13.3	8:12	2:3
14	7.5	5.5	2.0	40.0	26.7	13.3	4:21	1:5
15	12.8	11.4	1.4	40.0	26 7	13.3	3:15	1:5
16	11.6	10.8	0.8	40.0	26.7	13 3	2:16	1:8
17	17.0	13.4	3.4	40.0	26.7	13 3	7:13	1:2
18	18.4	14.8	3.6	40.0	26 7	13.3	7:12	1:2

manganese as $Mn(SO_4)_2$,[27] a substance prepared chemically by reducing potassium permanganate with manganous sulphate and only stable in strongly acid solutions, hydrolyzing to manganese dioxide in weakly acid solutions. No proof could be adduced, however, of a reaction between the MnO_2 and Mn_2O_7 by adding the one to the other, as the concentrated acid necessary to hold the tetravalent manganese in solution was sufficiently strong to cause alone a slow evolution of oxygen from the heptavalent manganese. The two substances were then brought together in an oxidation-reduction cell, constructed as follows:

[27] Zeit. Elektrochemie, **11**, 853 (1905).

Two small porous cups were filled respectively with a solution of potassium permanganate containing 5% by weight of $KMnO_4$ and 15% by volume of concentrated H_2SO_4 and a solution of $Mn(SO_4)_2$. Each was tightly closed by means of a two-holed rubber stopper. Through one hole in each stopper projected a glass tube through which, by means of a platinum wire sealed in its end, connection was made with a wide coiled platinum foil electrode. Through the other hole a capillary tube led from the interior of the cup to a eudiometer dipping beneath water. The two cups were then placed in a vessel filled with 15% concentrated sulphuric acid. The electrical circuit was completed outside the cell through a millivoltmeter. The course of the current through the external circuit was from the potassium permanganate compartment to that occupied by the manganese disulphate. The electromotive force generated produced a difference of potential between the poles of the cell of 0.1 volt.

In MnO_2 reduced Mn_2O_7, according to our hypothesis Mn_2O_5 should be the point of equilibrium between the two. Then in the cathode compartment of the cell we should have a reduction as represented by the equation

$$Mn_2O_7 + 2H_2 = Mn_2O_5 + 2H_2O,$$

occurring; and in the other compartment, the oxidation, as represented thus:

$$2Mn_2O_2 + O_2 = 2Mn2O_5.$$

As is represented by these equations, the oxygen consumed at one pole is equivalent to the hydrogen consumed at the other pole. We then have formulated per equivalent of electricity one part of Mn_2O_5 by the reduction and two parts by the oxidation. From the decomposition of the Mn_2O_5 to Mn_2O_4, we should then have evolved from the cathode compartment one volume of oxygen to two volumes from the anode compartment.

From the relative amounts of oxygen evolved from the two poles, however, no evidence could be obtained to sho wthe occurrence of a reaction between the two manganese compounds.

The reduction of Mn_2O_7 by electrolysis directly to the instable Mn_2O_5 would account for the presence of oxygen in the cathode gases. Numerous arguments for the existence of pentavalent manganese can be found in the periodic system. The proximity

of this element to chlorine, bromine, etc., would lead one to expect the existence of Mn_2O_5, analogous to Cl_2O_5 and Br_2O_5, less stable than Mn_2O_7 just as Cl_2O_5 is less stable than Cl_2O_7. Four molecules of hydrogen would reduce two molecules of Mn_2O_7 to Mn_2O_5, according to the equation

$$\begin{aligned} 2Mn_2O_7 + 4H_2 &= 2Mn_2O_5 + 4H_2O \\ 2Mn_2O_5 &= 2Mn_2O_4 + O_2 \\ 2H_2 : O_2 &= 2 : 1. \end{aligned}$$

Two molecules of Mn_2O_5 breaking down to Mn_2O_4 would evolve one molecule of oxygen, making the ratio of oxygen evolved to hydrogen absorbed 1 : 2 a ratio frequently obtained experimentally.

The reduction of Mn_2O_7 to Mn_2O_6 and the subsequent decomposition of this oxide to the dioxide, according to the equations

$$\begin{aligned} Mn_2O_7 + H_2 &= Mn_2O_6 + H_2O \\ Mn_2O_6 &= Mn_2O_4 + O_2 \\ 2H_2 : O_2 &= 1 : 2 \end{aligned}$$

would yield a ratio of oxygen evolved to hydrogen absorbed of 2 : 1, a ratio in no instance realized experimentally. Besides, no reaction between manganate and permanganate could be found in which oxygen is evolved; the decomposition of manganates results in the formation of manganese dioxide and permanganate, as shown by the equation.

$$3Mn_2O_6 = Mn_2O_4 + 2Mn_2O_7,$$

an irreversible reaction in acid solution, the manganese dioxide precipitating, and the reaction therefore running to an end. With the tetravalent manganese present in a soluble form as $Mn(SO_4)_2$, the action should be reversible.

The cathode conditions in the electrolysis were probably favorable to the production of manganates, as the solution in direct contact with the cathode was no doubt alkaline from the formation there of KOH. The enveloping coat of manganese dioxide, playing the rôle of a diaphragm, would admit of slow diffusion of a manganate into the outer solution of acid permanganate. However, when these conditions were duplicated

as closely as possible, chemically and mechanically, no evolution of oxygen could be obtained.

Thus, were practically eliminated, assuming the accuracy of our observations, the hypothesis of a reduction by MnO_2 capable of an acceleration by the electrolysis and of a direct reduction of Mn_2O_7 at the cathode to either Mn_2O_5 or Mn_2O_6.

It now seemed evident that the elusive reaction must be a function of the diaphragm formed by the heavy, compact coat of manganese dioxide enveloping the cathode. The complications incident thereto were accordingly eliminated by the use of a rapidly rotating cathode.

The cathode was attached to a rotating device.[28] Its stem projected through a mercury seal into a porous cup. The cup was tightly closed with a rubber stopper containing three holes. Through a central hole projected a glass tube, through which worked the shaft of the rotating cathode; surrounding this tube was the annular-shaped, mercury cup, formed from a glass tube of larger diameter, supported by a closely fitting rubber stopper and blown out at its upper end into a hemisphere with inturning edges. Dipping into the mercury cup from above was another glass tube, sealed at its upper end to the stem of the cathode. By this means, the cathode was allowed to rotate freely through an air-tight mercury joint, capable of withstanding any pressure, depending on the height of the mercury column. Through a second hole in the stopper projected a glass tube for introducing solutions into the cup, bearing a stopcock and, on its upper end, a thistle-top funnel. Connection was made through the third hole, by means of a capillary tube, with a eudiometer. As anode was employed, a broad platinum plate surrounding the porous cup. A gas coulometer was joined in series, and after the cell had been partially filled with sulphuric acid of the desired strength, the current was turned on, with cathode rotating, to test the tightness of the cathode compartment. The required amount of potassium permanganate in saturated solution was then added through the funnel tube in sufficient amount to bring the concentration of the cathode solution up to the desired point, and the electrolysis was continued.

With rotating cathode, which precluded the possibility of the

[28] Cf. Löb. Zeit. Elektrochemie, 7, 118 (1900).

formation of a coating of manganese dioxide, even at high current densities no gas was evolved, showing a quantitative reduction of the permanganate to a stable form. Manganese dioxide was formed as before. With stationary cathode, under the same conditions of current density, gas was evolved, thus establishing the correctness of the hypothesis that the manganese dioxide diaphragm was responsible for the anomolous evolution of oxygen from the cathode. It seems quite possible that the manganese dioxide diaphragm may act like a bipolar electrode, but we have no experimental proof of this.

At various times during the work with $KMnO_4$, the odor of ozone was noticed. This odor being particularly strong in the gas from the enclosed cathode compartment used in the last experiment, a sample of this gas was subjected to qualitative tests for ozone by the method of Keiser and McMaster.[29] Potassium iodide was instantly oxidized by it. The absence of peroxides which could scarcely be evolved from a solution of $KMnO_4$ was demonstrated by the non-appearance of a blue color on bubbling the gas through a solution of potassium ferricyanide and ferric chloride.

This work was suggested by Professor Bancroft. Its completion was made possible amid numerous distractions only by his constant interest and assistance. The author takes this opportunity of expressing to him his thanks and appreciation.

Cornell University,
April, 1908.

DISCUSSION.

Mr. F. A. Lidbury: It occurs to me that one possible explanation of the phenomenon mentioned in the paper may lie in the fact that here we have almost the same sort of a case as would give the ideal conditions for the production of hydrogen di-oxide, as was quoted by Dr. Bancroft in his lecture the other evening. The case he mentioned was that of an oxygen electrode employed as a cathode, whereas here you have a case of

[29] Am. Chem. Jour. 39, 96 (1908).

electrolysis with a cathode on which is a deposit of manganese di-oxide. I do not know whether you could get, under any circumstances in the case of electrolysis with such a cathode, an appreciable quantity of hydrogen di-oxide. It is obvious that if that could take place, or if you could have even a momentary formation of hydrogen di-oxide, that would at once react with the acid permanganate in solution and give oxygen off. I cannot quite see what experiments could be carried out to test that hypotheses, but I offer it as a possible explanation, and one which does not involve the conception of what really amounts to an anode and cathode on the same surface.

Mr. Anson G. Betts: I should like to suggest a form of cell with which you could do away with both oxygen and hydrogen evolution from solutions ordinarily producing them on electrolysis. If a bipolar electrode of very thin platinum pervious to hydrogen should be placed in a sodium sulphate solution, the hydrogen liberated on one side should be absorbed by the platinum, and pass through and combine with the oxygen on the other side. This would give sulphuric acid and caustic soda, without evolution of gas. Would hydrogen pass through ordinary platinum, if very thin?

Dr. Bancroft: It seems to me that Mr. Lidbury's explanation is an excellent one. Of course, it may be wrong, but it strikes me as greatly more probable than the tentative explanation that I offered of the manganese di-oxide acting as a bi-polar electrode.

As regards the case of a bi-polar electrode acting as a depolarizing diaphragm, we realized that experimentally a number of years ago, in a paper presented at one of the New York meetings. With a rotating diaphragm hydrogen or metal, was precipitated theoretically on one side, and oxygen on the other. We showed that under these circumstances the current goes through the diaphragm, and that there was no polarization. That was due to the rotating diaphragm instead of this infinitesimally thin one Mr. Betts suggested.

A paper read by Dr. W. D. Bancroft at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., April 30, 1908; President C. F. Burgess in the Chair.

ELECTROLYSIS OF NITRIC ACID USING A MERCURY CATHODE.

By J. A. Wilkinson.

When the electric current is used as a means of bringing about a chemical action, it was formerly believed that there was some mysterious effect due to the current itself. This idea is being overcome, and the fact is now realized that the only action of the current is to tend to set free ions at the electrodes, and that any chemical action that takes place will be between these ions or other substances in the solution. If the ions could be set free in any other way, then the same chemical action would take place without the presence of the current. In other words, if we have the same conditions, no matter how obtained, the same chemical action will result.

The product of the action of nitric acid on mercury is nitric oxide, but when a solution of nitric acid is electrolyzed with a mercury cathode, the reduction product is not nitric oxide, but hydroxylamine. It was the object of these experiments to find the reason for this difference between the electrochemical and chemical action. Tafel[1] has used this as an example to show that there is some essential difference due to the electric current.[2]

A similar case to this is that of copper and nitric acid. Under ordinary conditions, copper dissolves in nitric acid to give off nitric oxide, but when nitric acid is electrolyzed with a copper cathode, the reduction product is ammonia, and not nitric oxide. Turrentine,[3] in a series of experiments in this laboratory, has shown that in the case of copper, the difference between the electrochemical and chemical action is due to the fact that the conditions are not identical. When copper dissolves in nitric

[1] Zeit. anorg. Chemie, **31**, 290 (1902).
[2] Bancroft, Jour. Phys. Chem., **12**, 111 (1908).
[3] Jour. Phys. Chem., **10**, 715 (1906).

acid, there is a high concentration of copper as ion around the copper strip, and the nitric acid is reduced in the presence of copper ions. When the nitric acid is electrolyzed with a copper cathode, there is practically no copper present as ion, and the nitric acid is reduced in the absence of copper ions. Turrentine has shown that when copper ions are present, the reduction product is nitric oxide, and not ammonia. When using a copper anode, ammonia was formed, until the copper that had dissolved from the anode had moved across to the cathode, but after that, nitric oxide. Turrentine showed, further, that if the copper ions were removed in any way during the solution of copper in nitric acid, the product is ammonia. These experiments showed, therefore, that the difference between the two actions was simply the difference in the conditions, that is, the presence of copper ion.

Similar experiments have been tried with mercury. A solution of nitric acid and sulphuric acid, 10 per cent. of the former and 50 per cent. of the latter, was used as an electrolyte, this being the solution used by Tafel. A platinum wire served as anode, and the cathode was mercury, contained in a small funnel tube bent in the form of a deflagrating spoon. The cathode was placed in a porous cup, closed with a rubber stopper, with a delivery tube for collecting the gas evolved. The surface of the mercury exposed to the solution was covered with a layer of mercurous sulphate, thus insuring the presence of mercury ions at the cathode. The current density was 0.5 amperes per square centimeter.

The evolved gas turned brown on mixing with air, showing the presence of nitric oxide. When analyzing the gas, the nitric oxide was absorbed in ferrous sulphate solution.

Volume of gas.	NO.	NO.
cc	cc	
62.8	39.2	60%
59.8	37.3	62%
99.5	45.5	46%
99.6	78.6	79%
58.2	34.6	59.4%

The gas thus contained on an average about 60 per cent.

nitric oxide, and agrees with the case of copper that the presence of the metal ion around the cathode gives nitric oxide on electrolysis, and not hydroxylamine, as is ordinarily obtained.

The next step was to cause the chemical action to give hydroxylamine, instead of the oxide. Mercury was allowed to drop from a capillary tube through a tube 15 inches long, containing the solution of nitric and sulphuric acids used before. This tube was the side arm of a larger tube, so that the mercury remained in contact with the nitric acid in the side arm only while it was falling through it. This also prevented the gases and products of reaction of the mercury and nitric acid, after it had fallen through, from mixing with those of the action in the side arm. This would keep down the concentration of the mercury ions in the side arm.

After the mercury had dropped through the solution for about twenty minutes, the contents of the side arm were poured into a small distilling flask containing lime. After standing a few minutes, the solution was heated to boiling, and the distillate tested for hydroxylamine. The contents required from one to five c.c. of N/10 potassium permanganate solution, the amounts depending on the time the mercury was allowed to fall through the solution. This method eliminated the presence of nitrites and mercurous salts that might be formed and would act on the permanganate if titrated direct.

The results show the presence of small amounts of hydroxylamine and that the chemical action and the electrochemical actions are the same when the metal ions are absent.

SUMMARY.

It has been shown that when nitric acid acts on mercury in the presence of mercury as ion, the product is nitric oxide, whether done by electrolysis or straight chemical action.

When nitric acid acts on mercury in the absence of the metal as ion, the product is hydroxylamine, whether done electrolytically or chemically.

This work was suggested by Prof. Bancroft and has been carried on under his supervision.

Cornell University.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., April 30, 1908; President C. F. Burgess in the Chair.

COPPER ANODES IN CHLORIDE SOLUTIONS.

By Saul Dushman.

In the following paper I intend to give a summary of an investigation undertaken with the object of explaining the anomalous behavior of copper as anode in chloride solutions. Preliminary experiments showed that copper dissolved with a valency ranging from 1 to 2, according to the experimental conditions. It was observed that in concentrated hydrochloric acid solution, it dissolved as a univalent metal, while in more dilute solution the valency was greater, and finally attained a value of 2 for very dilute solutions. The particular concentration of hydrochloric acid at which the copper ceased to dissolve as purely univalent varied with the rate of stirring, rate of circulation, current density, and other factors. Increased stirring or circulation caused the metal to dissolve much more as cuprous, while increasing the current density, under otherwise constant conditions, increased the proportion of cupric.

Although several hypotheses could have been made to explain these experiments, the one chosen seems to be in best accord with the quantitative experiments described below. It is assumed that the copper anode dissolves by the action of the current in such a manner that, at the boundary between solution and electrode, the chemical equilibrium between the cupric and cuprous salts in hydrochloric acid solution is maintained.

The investigation therefore naturally divided itself into two parts: (a) Investigation of the chemical equilibrium, (b) determination of concentrations at the electrode in the electrolytic experiments. The chemical equilibrium between cuprous and cupric salts has been investigated by E. Abel,[1] R. Luther,[2]

[1]E. Abel, Zeit. f. Anorg. Chem., **26**, 361.
[2]R. Luther, Zeit. f. Physik. Chem., **36**, 385.

and Bodländer and Storebeck.[3] A large number of experiments performed by myself, in which the methods of analysis and manipulation were different from any of the above, proved in conformity with those of the last named authors. The equilibrium between copper, cupric and cuprous salts in presence of hydrochloric acid is represented by two equations:

$$\overset{\circ}{Cu} + \ddot{Cu} \rightleftharpoons 2\,\dot{Cu} \qquad (1)$$

$$\dot{Cu} + 2\,\acute{Cl} \rightleftharpoons Cu\,\acute{Cl}_2 \qquad (2)$$

Bodländer and Storbeck determined the values of the constants $k_1 = (\ddot{Cu})/(\dot{Cu})^2$ and $k_2 = (Cu\acute{Cl}_2)/(\dot{Cu})(\acute{Cl})^2$ as 1.4×10^4 and 4×10^4, respectively, concentrations being in mols per litre.

The second part of the investigation had for its object the determination of the concentration at the anode during the electrolytic experiments, so that the values of k_1 and k_2 might be calculated from these and compared with those obtained from the equilibrium experiment. Fig. 1 is a diagram of the electrolytic cell used. It consisted of two porous cylinders, P_1 and P_2, between the ebonite discs, E E, two concentric glass cylinders, L and M, also held between ebonite discs, and a rotating copper anode, A, making contact with a shaft and holder, H. To prevent liquid from entering within the anode tube, two ebonite plugs (the lower of these having a glass Tip, T) were provided with threaded holes, so that they could be tightened against the copper, as shown in the diagram. The tube could therefore be taken off the plugs and weighed. Its area was about 40 square centimetres. A rubber tube, with stopper, S, fitted over the upper plug. The electrolyte entering B passed between the two porous cylinders, through holes in the center disc, E, and the glass cylinder, M, and up and around the anode, leaving by means of the exit tube, D. The cathode consisted of a platinum gauze, C, attached around the discs E. The different parts were cemented together. Cork wedges between the discs and the glass container, F, prevented any lateral motion of the discs when the anode was set rotating.

Since hydrochloric acid containing air in solution dissolves

[3] G. Bodländer and O. Storbeck, Zeit. f. Anorg. Chem., 31, 1. 458.

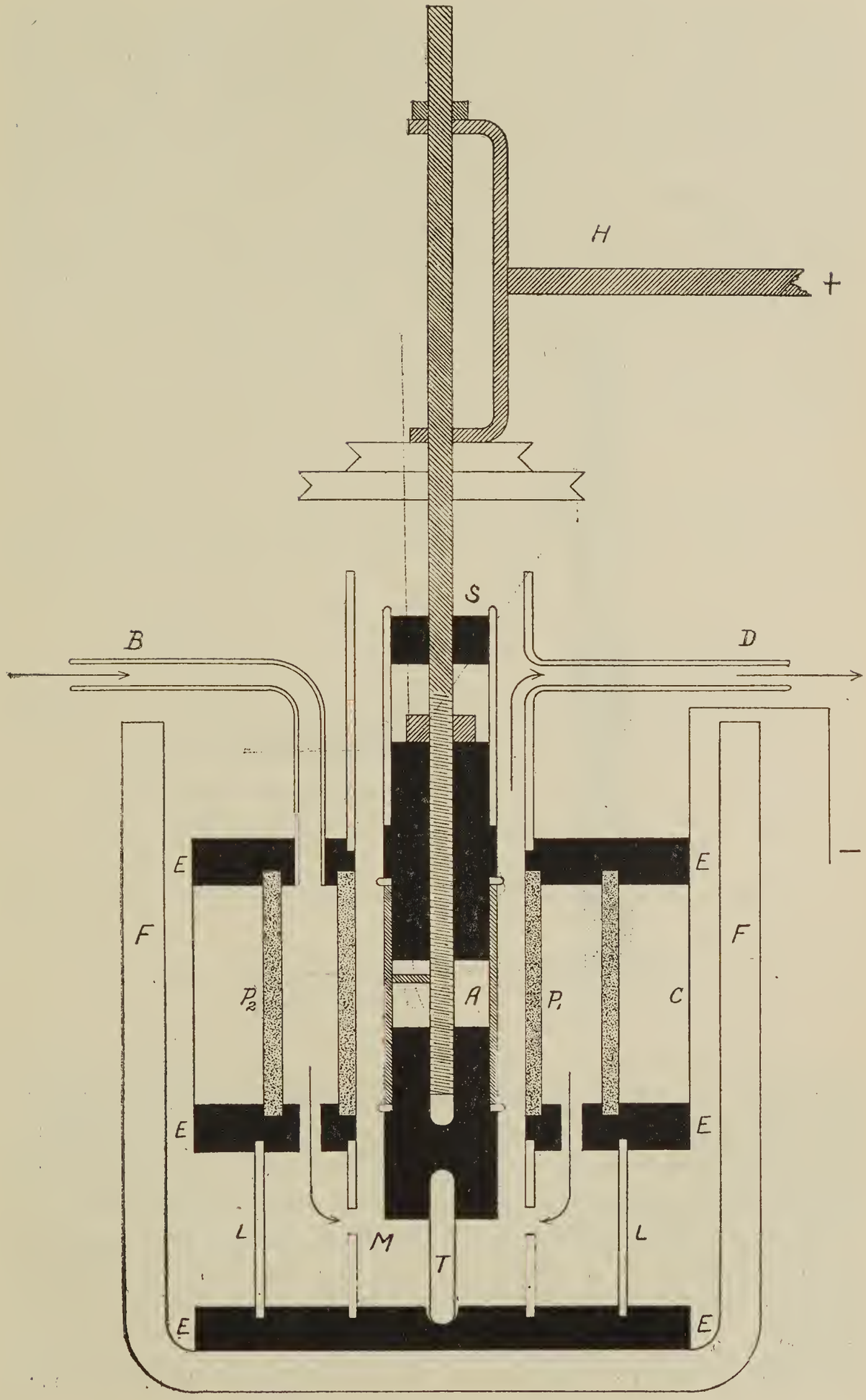

FIG. 1.

copper even without current, the solution to be electrolyzed was always freed from air by exhaustion, and then saturated with carbon dioxide. Blank experiments showed that in such a solution the copper dissolved only very slightly. A large bottle filled with stock solution was permanently connected with a carbon dioxide generator, and as the solution ran out into the cell, the gas took its place. After circulating through a cell once, the electrolyte passed into a measuring cylinder, and was then

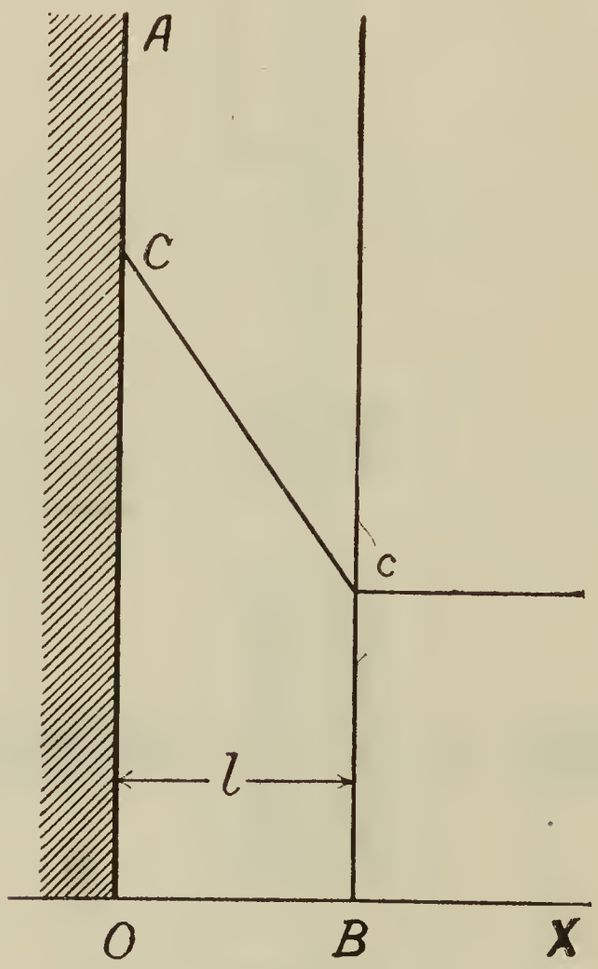

FIG. 2.

discarded. A copper coulometer and ammeter were placed in series with the cell. During the experiment, the rates of circulation and stirring were kept nearly constant, the average speed of rotation being about 1,500 per minute in all the experiments.

Now we shall consider how, by means of such an arrangement, we can calculate, in a simple manner, the concentrations at the electrode, for these are evidently different from those in the solution at a distance from the electrode.

In Fig. 2, let OA represent a section of the electrode, whose

area is S. Let OX represent the distance from the electrode. It has been shown by Nernst and Brunner that in a rapidly stirred solution the diffusion is limited to a very thin layer close to the electrode, the thickness L decreasing with increasing rate of rotation. Outside this layer, the solution is of uniform composition. The concentrations of $\ddot{C}u$, for example, at the electrode and in the solution are represented by OC and Bc, respectively. Owing to the circulation of the electrolyte, the concentration in the solution rapidly attains the constant value Bc, and the distribution of concentrations in the layer is given by the line Cc. Now since all the concentrations remain constant during the electrolysis, it is evident that the following relation exists between OC and Bc:

The amount of cupric ion entering the layer in any time is equal to the amount diffusing out into the solution, together with the amount transported in the same time, Or

$$\frac{a\,i\,t}{2 \times 96540} = \frac{D\,S\,t\,(C-c)}{L} + \frac{n\,i\,t}{2 \times 96540}$$

where a = fraction of current used to produce cupric ion,
i = current in amperes,
t = time in seconds,
D = diffusion constant in cms/sec.,
n = transport number of ion in the solution.
Since c = ait/2 × 96,540 V where V = volume in cc.,

$$C = \frac{a\,i\,t}{2 \times 96540}\left(\frac{1}{V} + \frac{L\,(1-n)}{D\,S\,t}\right)$$

Similar equations hold for the other ions in the solution.

The thickness of the layer was determined by two different methods, and both gave approximately the same result. It was about 6×10^{-4} cms. The diffusion constants were calculated from the mobilities by means of Nernst's formula as modified by Bose. The fall in concentration in the layer was found to be very large. Thus, in one experiment with N/200HCl, the concentration of $\ddot{C}u$ at the electrode was 0.8×10^{-3}, while in the solution it was 0.3×10^{-3}. In different experiments, in

which the concentrations of HCl, $\ddot{Cu}$, $\dot{Cu}$ and $CuCl_2$ varied, the value of the constant $k_1 = (\ddot{Cu})/(\dot{Cu})^2$ was nevertheless very fair, being about 0.3×10^4, instead of 1.4×10^4, as determined by Bodländer and Storbeck.

However, considering the various assumptions on which these calculations have been made, I consider the agreement fair. Experiments are still in progress by which I hope to obtain more accurate results, but the data so far obtained seem to emphasize this point: By the assumption of instantaneous equilibrium at the boundary between anode and solution, the apparently erratic results are reduced to agreement with Faraday's Law.

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A paper read by title at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., April 30, 1908, President C. F. Burgess in the Chair.

THE SOLUBILITIES OF BORIC, CAMPHORIC, BENZOIC AND SALICYLIC ACIDS IN AQUEOUS ETHYL ALCOHOL SOLUTIONS AT 25°

By Atherton Seidell.

The results here reported were obtained in the course of an extended series of determinations of the solubilities of those compounds in the United States Pharmacopœia for which the statements quoted therein could not be satisfactorily verified by a search through the solubility data published in the better known chemical journals.[1]

All of the solubility determinations recorded in this paper were made under strictly identical conditions. A constant temperature water bath regulated accurately to 25° was used. The saturated solutions were prepared in all cases by mixing the solvent and the acid studied in thick walled test tubes of about 15-25 cc. capacity, closed with well-washed rubber stoppers. The test tubes were attached to a rotating frame immersed in the water bath and revolved upon the axis parallel to the diameter of the test tube at the rate of about 6 revolutions per minute. Equilibrium was assured in all cases by analyzing solutions which had been agitated for different lengths of time.

A sufficient quantity of each of the aqueous alcoholic solvents for all of the experiments was prepared at the beginning and the specific gravities of these solutions carefully determined by the pycnometer method. These determinations were made upon the solutions cooled to 15°. and the weight per cent. of absolute alcohol (C_2H_5OH) corresponding to each was read from the United States Pharmacopœia alcohol table.

The general plan of analyzing the saturated solutions was as

[1] For the available solubility data upon the acids here mentioned and also for references to the same, see Seidell's "Solubilities of Inorganic and Organic Substances" (D. Van Nostrand Co., New York, 1907), pages 58, 65, 104 and 274.

follows: At the end of the period of rotation the test tubes were placed in an upright position in the bath, with the stopper and a very little of the tube protruding, until the undissolved salt had settled upon the bottom. About 10-12 cc. of the supernatant clear solution was drawn into a pipette, having a cotton plug attached, through which the solution was filtered as it entered, the test tube itself not being removed from the bath until the portion of the saturated clear solution had been withdrawn for analysis. The solution in the pipette was then transferred to a pycnometer and its density accurately determined, after which it was either washed into a 200 cc. volumetric flask and diluted to the mark, or, in case the acid was one which could be determined by evaporating and weighing the residue, it was washed into a tared weighing bottle.

With those acids which could not be determined by drying and weighing, aliquot portions of the 200 cc. of solution in each case were analyzed by the procedure required for the particular acid.

The results in all cases were calculated to the grams of acid dissolved in 100 grams of the saturated solution. These figures were plotted on the abscissae and the weight per cents. of alcohol in the several solvents plotted on the ordinates in plates I and II section paper. The curve drawn through the several points represented the curve of solubility of the particular acid in aqueous alcoholic solutions of increasing content of alcohol. From this curve the figures corresponding to regular intervals of alcoholic strength of the solvent were read, and the molecular amounts of the constituents of the saturated solutions were then calculated.

BORIC ACID.

The sample of boric acid used for the present determinations was recrystalized from hot water and dried thoroughly. A weighed portion of it dissolved in water and aliquot portions of the solution mixed with equal volumes of glycerine and titrated with standard N/10 alkali, indicator phenolphthaleine, gave results corresponding to a purity of 99.9 % H_3BO_3.

Two series of determinations were made. In the first, the period of rotating the tubes in the thermostadt at 25° was 42 hours. The portions for analysis were withdrawn and the tubes containing sufficient solution were replaced and rotated together

with two newly-prepared tubes a second period of four days. The determinations in the two series agreed sastifactorily, showing that equilibriums had been reached during the first period of shaking.

The analyses of the solutions were made by titration of aliquot portions mixed with equal volumes of glycerine as mentioned above for the sample of boric acid itself. A correction for the c.c. of standard alkali required to neutralize the acidity of the glycerine was made in all cases.

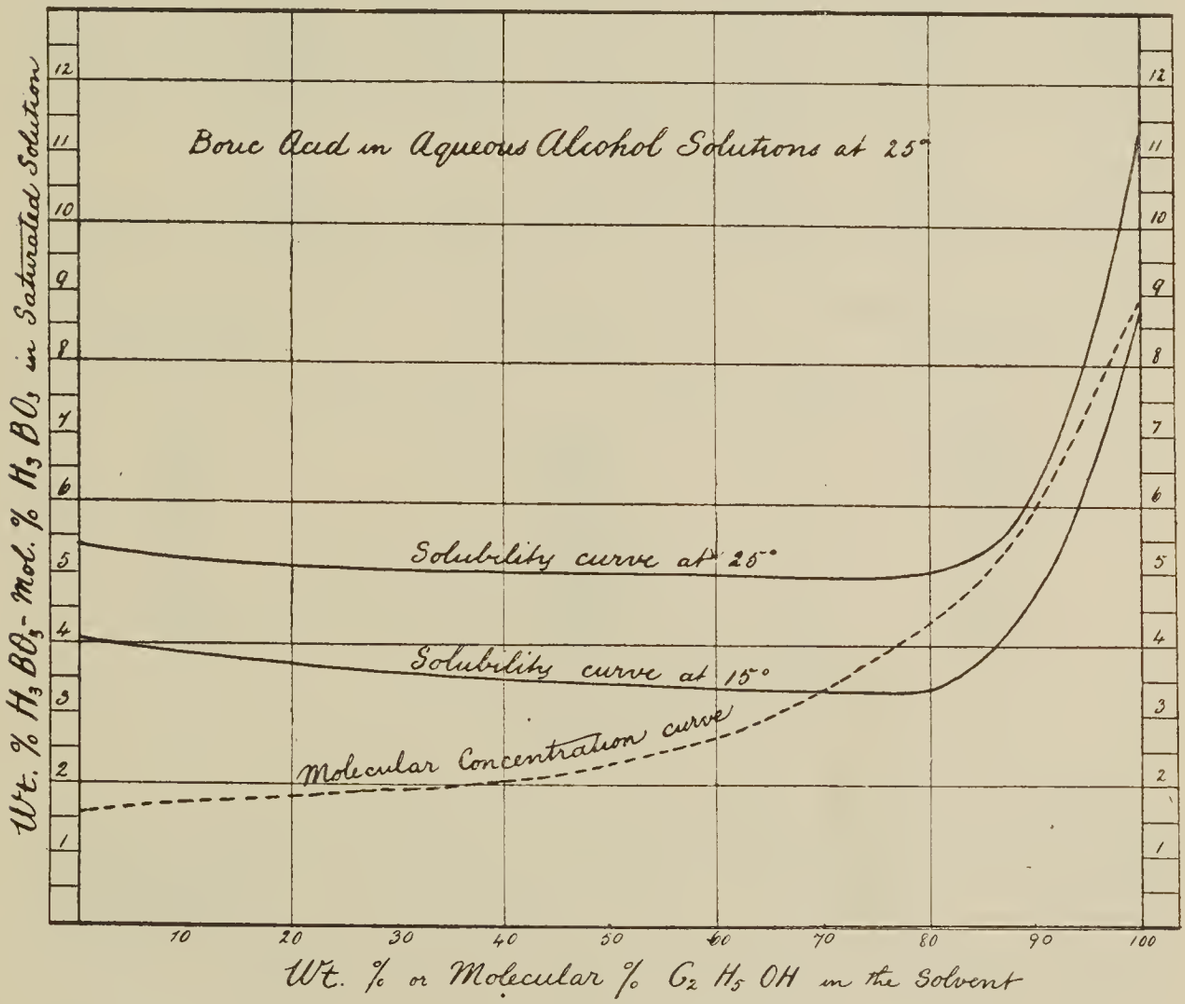

PLATE I.

An examination of the curve plotted on cross section paper from the results as determined and as calculated to the molecular basis show that in the first instance the grams of boric acid dissolved is somewhat less in alcoholic solutions of a strength not exceeding about 85 wt. per cent. than in pure water, but that above this concentration of alcohol, the amount of boric acid dissolved increases very rapidly. The curve therefore shows a minimum between 80 and 90 wt. per cent. alcoholic strength. On

the other hand when the results are calculated to the molecular basis the solubility curve rises very gradually throughout its whole length.

Before the constant temperature shaking apparatus used for the other results reported in this paper had been completed, a series of determinations was made at 15° by keeping the solutions in a room maintained at 15° C. over long periods of time and shaking at intervals by hand. The results yielded a fairly uniform curve after about one month's time, but it is, of course, not certain that final equilibrium had been reached. The results which were obtained are believed to be of some interest although it is realized that absolute accuracy can not be claimed for them. They are therefore given in the following table.[2]

Solubility of H_3BO_3 in Aq.C_2H_5OH Solutions at 15°.

Weight per cent. Alcohol in Solvent.	Sp. Gr. of Sat. Solution at 15°.	Grms. H_3BO_3 per 100 Grms. Sat. Solution.
0.0	1.014	4.11
8.9	0.9986	3.90
32.0	0.9658	3.58
51.0	0.9268	3.48
70.2	0.8820	3.22
91.3	0.8389	5.06
93.6	0.8370	5.70
99.8	0.8356	9.18

TABLE I.

Solubility of Boric Acid in Aqueous Alcohol Solutions at 25°.

No.	Solvent.		Sp. Gr. Sat. Solutions at 25°.		Grms. H_3BO_3 per 100 Grms. Sat. Solution.	
	Sp. Gr. at 15°.	Wt. % C_2H_5OH.	Series 1	Series 2	Series 1	Series 2
1	Dist. H_2O	0.0	1.019	1.018	5.44	5.41
2	0.9856	8.9	1.003	1.002	5.24	5.21
3	0.9545	32.0	0.967	0.967	5.17	5.15
4	0.9164	51.0	0.929	0.930	5.19	5.19
5	0.8718	70.2	0.885	0.885	5.01	4.98
5 (a)	0.8401	83.0	. . .	0.855	. . .	5.21
5 (b)	0.8279	88.0	. . .	0.847	. . .	5.73
6	0.8184	91.4	0.841	. . .	6.74	. . .
7	0.8125	93.6	0.838	. . .	7.40	. . .
8	0.8048	96.3	0.838	0.838	8.95	8.89
9	0.7941	99.8		8.838	11.16	11.18

[2] The author is indebted to Mr. J. H. Shrader, of this laboratory, for making these determinations.

These results plotted on cross section paper yielded a curve from which the following figures were read or calculated.

Wt. % C_2H_5OH in Solvent.	Sp. Gr. of Sat. Solution at 25°.	Grms. per 100 Grms. Sat. Solution.			Molecular Concentrations.	
		H_2O.	H_3BO_3.	C_2H_5OH.	Mol. % C_2H_5OH in Solvent (C).	Mol. % H_3BO_3 in Sat. Solution (C).
0	1.018	94.58	5.42	00.0	0.00	1.641
20	0.987	75.84	5.20	18.96	8.91	1.782
40	0.952	56.94	5.10	37.96	20.68	2.023
60	0.908	48.00	5.00	57.00	37.84	2.025
80	0.862	19.00	5.05	75.96	61.01	2.899
85	0.853	14.2	5.30	80.50	68.95	3.260
90	0.842	9.4	6.20	84.4	77.89	4.075
95	0.838	4.6	8.00	87.4	88.14	5.653
100	0.838	0.0	11.20	88.8	100.00	9.426

$H_2O=18.02$ $C_2H_5OH=46.05$ $H_3BO_3=62.02$

No. of gram-molecules of H_2O present = grams of $H^2O \div 18.02$
" " " " " C_2H_5OH " = " " $C_2H_5OH \div 46.05$
" " " " " H_3BO_3 " = " " $H_3BO_3 \div 62.02$

Therefore

$$c = \frac{\text{No. grm. mol. } C_2H_5OH}{\text{No. grm. mol. } H_2O + \text{No. grm. mol. } C_2H_5OH}$$

$$C = \frac{\text{No. grm. mol. } H_3BO^3}{\text{No. grm. mol. } H_2O + \text{No. grm. mol. } C_2H_5OH + \text{No. grm. mol. } H_3BO^3}$$

This curve plotted on the diagram with the 25° results shows an even greater depression of the solubility in moderately concentrated alcoholic solutions than does the 25° curve. Whereas 4.11 grams H_3BO_3 are contained in 100 grams of the saturated aqueous solution only 3.22 grams are present in the 70% (by wt.) alcohol solution, a difference of 0.89 grams. The same difference for the 25° results is 0.43 grams.

In the same manner as the 15° determinations were made, a series of tubes were placed in the 37° constant temperature room and shaken at intervals by hand for as long as four months. Although the amount of boric acid dissolved in the aqueous solution and more dilute alcoholic solutions did not change appreciably, constant results for the solutions of higher percentages of

alcohol could not be obtained. The figure for the solubility of H_3BO_3 in H_2O at 37° was found to be 7.09 grams per 100 grams saturated solution. The sp. gr. of solution at 37° was 1.024.

CAMPHORIC ACID.

The sample of camphoric acid used bore the label—Acid Camphoric, Merck, Highest Purity, Medicinal. A melting point determination showed it to soften at 179° and then gradually melt around the edges until the melting was complete at 185°. The physical appearance was all that could be desired; pure white crystalline powder. The alcoholic solution was lævorotatory. One gram dissolved in 250 c.c. water, and aliquot portions of the solution titrated with N/10 KOH using phenolphthaleine gave results showing the sample to be 99.7 per cent. pure $C_8H_4(COOH)_2$.

Table II.

Solubility of Camphoric Acid in Aqueous Ethyl Alcohol Solutions at 25°.

Experimental Determinations.

No.	Solvent.		Sp. Gr. Sat. Solutions at 25°.	Grms. $C_8H_{14}(COOH)_2$ per 100 Grms. Sat. Solution.
	Sp. Gr. at 15°.	Wt. % C_2H_5OH.		
1	Dist. H_2O	0.0	1.00	0.754
2	0.9856	8.9	1.00	1.239
3	0.9545	32.0	1.00	16.29
4*	0.9164	51.0	1.00	38.61
5*	0.8718	70.2	1.00	48.95
6*	0.8401	83.0	0.985	51.46
7*	0.8189	91.4	0.980	51.13
8	0.8048	96.3	0 970	50.37
9	0.7941	99.8	0.960	50.13

Calculated Determinations.—The above results plotted on cross section paper gave a curve from which the following figures were read or calculated.

Wt. % C_2H_5OH in Solvent.	Sp. Gr. of Sat. Solution at 25°.	Grms. per 100 Grms. Sat. Solution.			Molecular Concentration.	
		H_2O.	$C_8H_{14}(COOH)_2$	C_2H_5OH.	Mol. % C_2H_5OH in Solvent (c).	Mol. % $C_8H_{14}(COOH)_2$ in Sat. Solution (C).
0	1.00	99.25	0.754	0.0	0.00	0 0684
10	1.00	88.56	1.60	9.84	. . .	. . .
20	1.00	74.96	6.30	18.74	8.91	0.6645
30	1.00	60.20	14.00	25.80	. . .	. . .
40	1.00	44.4	26.00	29.6	20.68	4 016
50	1.00	31.0	38.00	31.0	. . .	. . .
60	1.00	22.0	45.00	33.0	37.84	10.40
70	1.00	15.3	49 00	35.7	. . .	. . .
80	0.995	9.76	51.20	39.04	61.01	15.56
90	0.980	4.86	51.40	43.74	77.98	17.40
100	0.960	0.0	50.10	49.90	100.00	18.77

The molecular concentrations (c) and (C) were calculated as shown in Table I.

Two series of determinations were made at widely separate dates; the first in December and the second in March. The lengths of time of rotation were respectively 6 and 4 days; the determinations marked with an asterisk in the table belonged to the second series, the others to the first series.

The dissolved camphoric acid was determined by evaporating the weighed portions of the saturated solutions to dryness in weighing bottles and drying the residues to constant weight in the water oven at about 99° C. An experiment made by drying a few grams of the salt successive periods of time in the same oven showed that the loss in weight after each period was negligible. The analytical results which were obtained are given in Table II., and the solubility and molecular concentration curves shown in Plate II.

BENZOIC ACID.

The benzoic acid used for the determinations was marked "Benzoic Acid from Benzoic Resin, English." The melting point was 120°. By titration of weighed portions of the sample dissolved in dilute alcohol with standard alkali, using phenolphthaleine as indicator a purity corresponding to practically 100 per cent. was found.

Two series of determinations were made at different times. The durations of the rotations were respectively 7 and 4 days. The analyses of the diluted solutions were made by titration with standard alkali. The tabulated results are given in Table III. and the curves plotted from them shown on Plate II.

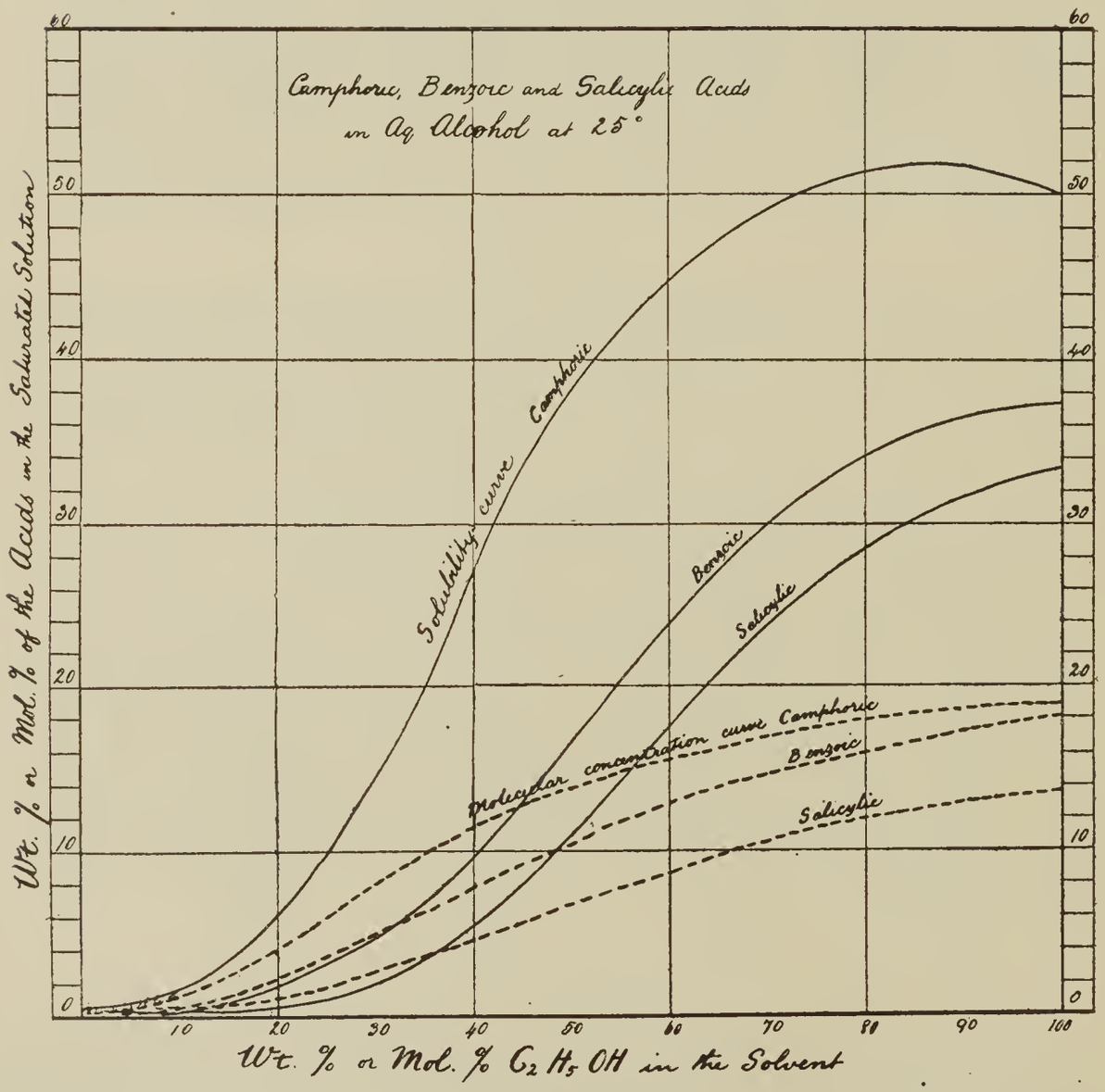

PLATE II.

TABLE III.

Solubility of Benzoic Acid in Aqueous Ethyl Alcohol Solutions at 25°.

Experimental Determinations.

No.	Solvent.		Sp. Gr. of Sat. Solution at 25°.	Grms. C_6H_5COOH per 100 Grms. Sat. Solution.
	Sp. Gr. at 15°.	Wt. % C_2H_5OH.		
1	Dist. H_2O	0.0	1.000	0.367
2	0.9856	8.9	0.987	0.581
3	0.9545	32.0	0.9574	4.677
4	0.9164	51.0	0.9464	17.80
5	0.8718	70.2	0.9404	30.07
6	0.8401	83.0	0.9311	35.05
7	0.8040	96.3	0.9128	36.51
8	0.7941	99.8	0.9093	36.91

Calculated Determinations.—The above results plotted on cross section paper gave a curve from which the following figures were read or calculated.

Wt. % C_2H_5OH in Solvent.	Sp. Gr. of Sat. Solution at 25°.	Grms. per 100 Grms. Sat. Solution.			Molecular Concentrations.	
		H_2O.	C_6H_5 COOH.	C_2H_5OH.	Mol. % C_2H_5OH in Solvent (c).	Mol. % C_6H_5 COOH in Sat. Solution (C).
0	1.00	99.63	0.367	0.0	0.00	0.0544
10	0.985	89.46	0.60	9 94	. . .	.
20	0.970	78.64	1.70	19.66	8.91	0.2898
30	0.959	67.27	3.90	28.83	. . .	. . .
40	0.951	54 54	9.10	36.36	20.60	1.917
50	0.946	41.5	17.00	41.5	. . .	. . .
60	0 943	30.48	23.80	45.72	37.84	6.772
70	0 940	21.1	29.7	49.21	. . .	. . .
80	0.934	13.2	34 0	52.8	61.01	12.91
90	0.922	6.4	36.0	57.6	77.89	15 52
100	0.908	0.0	36.9	63.1	100.00	18.08

The molecular concentrations (c) and (C) were calculated as shown in Table I.

SALICYLIC ACID.

The material used for the determinations was pure white crystals with melting point of 156°. By titration with standard alkali it corresponded to 100 per cent. purity. Only one series of deter-

minations was made, but in this series the tubes were rotated at 25° for three days, and there can be no doubt that equilibrium had been reached. The analyses were made by titrating aliquot portions of the solutions with standard alkali using phenolphthaleine as indicator. The results obtained are shown in Table IV., and the curves in Plate II.

TABLE IV.

Solubility of Salicylic Acid in Aqueous Ethyl Alcohol Solutions at 25°.

Experimental Determinations.

No.	Solvent.		Sp. Gr. of Sat. Solution at 25°.	Grms. $C_6H_4OH.COOH_2$ per 100 Grms. Sat. Solution.
	Sp. Gr. at 15°.	Wt. % C_2H_5OH.		
1	Dist. H_2O.	0.00	1.001	0.22
2	0.9856	8.90	0.986	0.336
3	0.9545	32.00	0.957	2.68
4	0.9164	51.00	0.945	12.82
5	0.8718	70.2	0.941	24.01
6	0.8279	88.0	0.932	31.03
7	0.8048	96.30	0.923	32.45
8	0.7941	99.80	0.919	33.20

Calculated Determinations.—The above results gave a curve from which the following figures were read or calculated.

Wt. % C_2H_5OH in Solvent.	Sp. Gr. of Sat. Solution at 25°.	Grms. per 100 Grms. Sat. Solution.			Molecular Concentrations.	
		H_2O.	C_6H_4OH $COOH_2$	C_2H_5OH.	Mol % C_2H_5OH in Solvent (c).	Mol. % C_6H_4OH $COOH_2$ in Sat. Solution (C).
0	1.001	99.78	0.22	0.00	0.00	0.0288
10	0.984	89.66	0.38	9.96	. . .	. .
20	0.970	79.36	0.80	19.84	8.91	0.1198
30	0.959	68.46	2.20	29.34	. . .	. .
40	0.951	56.46	5.90	37.64	20.60	1.070
50	0.945	43.90	12.20	43 90	. . .	. . .
60	0.943	32.68	18.30	49.02	37.84	4.404
70	0.941	22.8	24.00	53.2		. . .
80	0 937	14 34	28.30	57.36	61.01	8.774
90	0.930	6.86	31.40	61.74	77.89	11 67
100	0.919	0.00	32.20	67.8	100.00	13.69

The molecular concentrations (c) and (C) were calculated as shown in Table I.

The solubility of salicylic acid in aqueous ethyl alcohol solutions has been determined by Hoffman and Langbeck,[3] but these authors used only dilute solutions of alcohol. Their most concentrated solutions at 25° contained, in terms of molecular concentration, 2.8653×10^{-2} alcohol and 3.9253×10^{-4} salicylic acid. This highest concentration is below the strength of the second solution of the present series. It is noteworthy that in spite of the very short range of concentration covered by these authors their results yielded a line which, although nearly so, was not quite straight. The results shown here for salicylic acid give a wavy curve, which is nearer a straight line than the curves for benzoic and camphoric acids.

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[3] Zeit. physik. Chem., **51**, 400 (1905).

A paper read by A. T. Lincoln at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 2, 1908; President C. F. Burgess in the Chair.

ADDITIONAL EXPERIMENTS ON THE ELECTROLYTIC CORROSION OF BRASSES.

By A. T. Lincoln and G. C. Bartells, Jr.

In a previous paper[1] there were presented the results of an investigation on the electrolytic corrosion of brasses in normal solutions of a number of simple salts, including sodium chloride, sodium sulphate, sodium acetate, sodium nitrate, sodium carbonate, ammonium nitrate, ammonium oxalate and acid ammonium oxalate. It was the intention to determine the corrosion in solutions of mixtures of various salts, and particularly in sea water. In this paper we shall present the results obtained in the electrolytic corrosion of a number of brasses in synthetic sea water and in solutions of commercial bath salt.

The brasses employed were those prepared for the previous work and represented practically all of the stable solid solutions of copper-zinc alloys at 400° C., at which temperature they were annealed for several weeks, in order to insure equilibrium of these phases. For the preparation of these brasses, as well as for the details of the method employed in carrying out the electrolytic corrosion, reference must be had to the previous article.

In general, the method consisted in arranging the thirteen test pieces so that they could be corroded simultaneously. The brasses were the anodes and were rotated about 800 revolutions per minute, thus keeping the electrolyte thoroughly mixed. A current of about 0.03 ampere was passed through the solutions for about six to seven hours, and two copper coulometers were placed in series, and from these the current employed was ascertained. Platinum cathodes were used.

[1]Trans. of the Amer. Elec. Chem. Soc., XI., 43 (1907). Jour Phys. Chem., XI., 501 (1907).

Corrosion in Bath Salt Solution.

Solutions of commercial West India bath salt were prepared of approximately the concentration of sea water, *i. e.,* about 3.5 per cent. solutions. The corrosion was run in triplicate, and the data presented in Table I is characteristic. In the first column are given the percentage copper in the test pieces; in the second column, the number of grams the test pieces lost during corrosion; in the third column, the number of grams of copper in the corrosion product; in the fourth, the per cent. the copper found is of the total corrosion. While in the last column is given the so-called current efficiency, *i. e.,* the per cent. the copper and zinc dissolved was of the quantity that should have been dissolved by the current that was used.

TABLE I.

Per Cent. Cu in Test Pieces.	Grams of Corrosion.	Grams Cu in Corrosion.	Per Cent. Cu in Corrosion.	Current Efficiency.
3.08	0.2155	0.0017	.8	92.0
10.2	0.2096	0.0034	1.6	89.1
22.6	0.2083	0.0050	2.5	87.8
47.6	0.2026	0.0125	6 7	84.4
51.3	0.2565	0.0654	25.9	96.3
56.8	0.2827	0.0990	34 2	100.0
60.3	0.3302	0.2055	62.3	98.7
66.4	0.3420	0.2287	66.9	98.9
73.4	0.3595	0.2718	75.6	97.5
76.6	0.3664	0.2838	77.4	98.0
83.4	0.3901	0.3295	84.4	98.5
86.6	0.4019	0.3525	87.7	98.7
93.5	0.4249	0.4003	94.1	98.7

Copper deposited in Coulometer = 0.2268 g.

These results are represented diagrammatically in Fig. 1 by the curves designated "bath salt." The amount of corrosion decreases with the decrease of copper content, until brasses of about 53 per cent. are reached, when the corrosion remains practically constant for the remainder. The curve representing the copper in the corrosion shows that the corrosion product from the brasses, containing less than about 53 per cent. of copper, consists practically of pure zinc. This accounts for the film of pure copper which appears on the 51.3 per cent. copper

brass and which scales off readily. The per cent. of copper in the corrosion as represented in the next to the last column for the brasses containing α, β and α and β crystals is practically the same as in the test pieces, but with the appearance of the γ solid solutions, the copper apparently ceases to dissolve and the corrosion consists almost exclusively of the zinc. The current efficiency, as given in the last column for the brasses high in copper, represents that the copper and zinc dissolve almost quantitatively. Where the corrosion consists chiefly of zinc, the current efficiency is low. The current efficiency is calculated upon the basis that the copper dissolves as cuprous copper, and this has been confirmed in a series of experiments which we have carried out.

Corrosion in Synthetic Sea Water.

According to Dittmar,[3] the average of the total solids in the 160 samples of sea water collected by the Challenger Expedition is 3.5 per cent. He gives[4] the following average composition of the solids dissolved in sea water:

Chloride of sodium	77.758
Chloride of magnesium	10.878
Sulphate of magnesium	4.737
Sulphate of lime	3.600
Sulphate of potassium	2.465
Bromide of magnesium	0.217
Carbonate of lime	0.345
Total solids	100.000

This combination of acids and bases is an arbitrary one, and in the preparation of our sample of synthetic sea water, the same combinations were retained, except that the carbonate was potassium carbonate, instead of calcium carbonate. The calcium was introduced as additional calcium sulphate, the potassium required for the potassium carbonate being deducted from the potassium sulphate and the calcium sulphate substituted therefor. Otherwise, the sample of sea water was prepared

[3] Geol. History of Lake Lahoutan U. S. G. S. Monographs XI, Russel, Page 178.

[4] The Voyages of H. M. S. Challenger, Physics and Chemistry I, 204.

by employing the salts listed and the quantities taken sufficient to make a solution containing 3.5 per cent. of solids—the concentration of sea water.

The electrolytic corrosion was carried out in the manner previously described, and the data given in Table II are the results of one of the duplicate determinations. The headings of the columns are the same as in the other tables and are self-explanatory.

TABLE II.

Per Cent. Cu in Test Pieces.	Grams of Corrosion.	Grams Cu in Corrosion C.	Per Cent. Cu in Corrosion.	Current Efficiency.
3.08	.2140	.0009	.45	92.2
10.40	.1858	.0012	.65	80.0
22.60	.2057	.0015	.73	88.6
47.6	.2118	.0031	1.5	90.8
51.3	.2513	.0405	16.1	100.0
56.8	.3040	.1428	46.9	101.4
60.3	.3295	.2044	62.0	99.4
66.5	.3424	.2243	65.6	100.8
73.4	.3619	.2660	73.5	100.5
76.3	.3679	.2720	76.1	101.8
83.2	.3917	.3251	83.0	100.9
86.6	.4020	.3459	86.0	101.0
93.6	.3485	.3239	93.0	82.5

Copper deposited in Coulometer = 0.2253 g.

The curve marked Synthetic Salt No. 1, in Fig. 1, represents diagrammatically the data given in Table II. These curves, as well as the others, have been smoothed, and while no values were obtained for brasses of compositions between 47 and 22 per cent. copper, the curves have been drawn continuous.

Another series of corrosions was run in a synthetic sea water, wherein iodine was substituted for bromine. The iodine was introduced as potassium iodide and the other necessary adjustments of the quantities of the constituents calculated so that a 3.5 per cent. solution was prepared. The data obtained from the results of these corrosions in this solution are represented by the series given in Table III.

TABLE III.

Per Cent. Cu in Test Pieces.	Grams of Corrosion.	Grams Cu in Corrosion.	Per Cent. Cu in Corrosion.	Current Efficiency
3.08	0.2647	0.0016	0.62	98.3
10.5	0.2173	0.0028	1.3	80.4
22.6	0.2538	0.0083	3.5	93.1
47.6	0.2613	0.0260	9.9	86.6
51.3	0.3488	0.1438	41.2	103.8
56.8	0 3535	0.1888	53.6	97.5
60.3	0.3804	0.2420	63.6	97.9
66.5	0.3774	0.2520	66.8	95.0
73.4	0.3781	0.2845	75.3	89.3
76.3	0.3805	0.2835	76.6	90.4
83.3	0.4081	0.3450	84.5	89.5
86.6	0.4092	0.3585	87.6	87.5

Copper deposited in Coulometer = 0.2612 g.

The curves labeled Synthetic Salt No. 2 represent diagrammatically, as do the other curves, the relation of the grams of corrosion, the grams of copper in the corrosion product, and the variation of these with the change in the concentration of the brasses. The vertical dotted lines represent the boundaries of the different solid solutions.

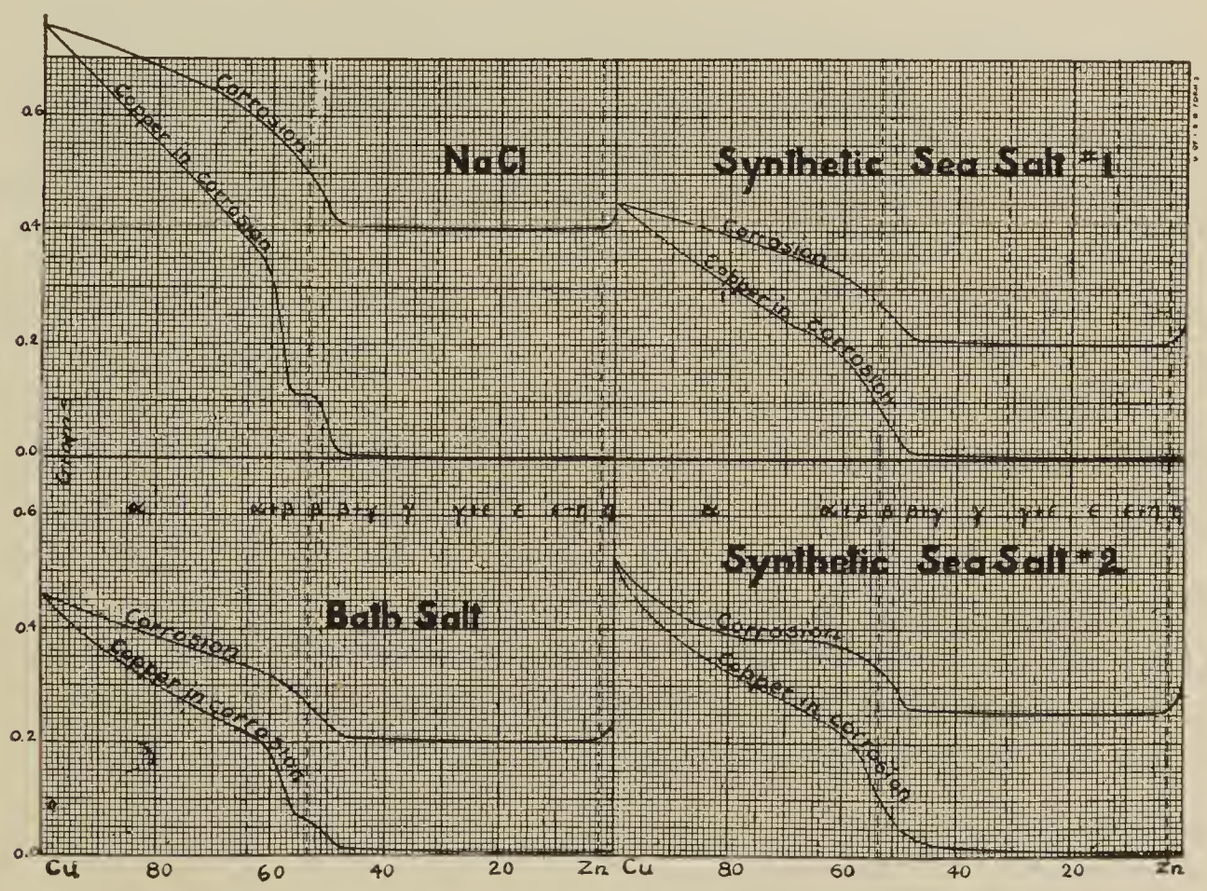


FIG. 1.

The upper curve in these diagrams represents a decrease in the amount of corrosion with the decrease in the copper content of the brasses. In some of the determinations, there seemed to by a tendency for the amount of corrosion of the sample of brass of the highest copper content to be lower than that found for brasses of lower copper content. In order to determine whether this was real or not, a number of determinations of the amount of corrosion of the three highest copper brasses were made in the two synthetic salts and the bath salt. The data given in Table IV represents the results of these numerous determinations.

TABLE IV.

Per Cent. Cu in Test Pieces.	Grams of Corrosion.		
	Synthetic Salt No 1.	Synthetic Salt No 2.	Bath Salt.
93.50	0.3681	0.3564	0.3713
86.60	0.3613	0.3483	0.3448
83.30	0.3460	0.3447	0.3379

These values show conclusively that the amount of corrosion increases with the increase in the copper content of the brass.

In Fig. 1 is given, for comparison, the curves for the corrosion of the brasses as determined in normal sodium chloride solutions. It will be readily observed that the general form of these curves, representing the grams of corrosion in the sodium chloride solution, is the same as that for the synthetic sea waters and for the bath salt solutions. The curve representing the grams of copper in the corrosion product is similar in all four cases. With the appearance of the γ crystals, the copper in the corrosion product drops nearly to zero, and for the brasses, the copper content of which is less than about 53 per cent. copper, the corrosion product is practically pure zinc. Therefore, we may conclude that the corrosion of these samples of brasses is practically the same in the synthetic sea water and in solutions of bath salt as in pure sodium chloride solutions.

Urbana, Illinois,
May 21, 1908.

DISCUSSION.

PROF. J. W. RICHARDS: I would ask whether Prof. Lincoln kept the cathode products away from the electrode which was corroded electrolytically. Were the products formed at the cathode allowed to accumulate in the solution so that it became progressively more alkaline, and thus changed the electrolyte? That would make the conditions different from the original electrolyte.

PROFESSOR LINCOLN: The experiment was performed in a beaker in which the anode rotated several hundred revolutions per minute, and the liquid, of course, was thoroughly stirred, and the anode and cathode products were thoroughly mixed.

PROFESSOR RICHARDS: Therefore the results would not apply to the corrosion of the metals in sea water where the cathode products are not present to any perceptible concentration.

PROFESSOR BANCROFT: I differ with the conclusion, because with the substances which are found in sea water, of course, you will always have a tendency for things to be alkaline, and then there is the other point which Prof. Richards has not taken into account, that there is a difference in the character of the alloys in the electrodes—you do not get the degree of alkalinity in the aluminum alloys. That is a possible difference which is not always taken into account.

PROFESSOR RICHARDS: I can see the value of the experiments as showing the relative corrodibility of different alloys in the electrolyte as used, but in actual sea water the amount of electrolyte is practically infinite, whereas in the beaker it is small, and therefore you do not have that change in the composition of the sea water which Prof. Lincoln must have had in the composition of the liquids in his beakers.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., April 30, 1908; President C. F. Burgess in the Chair.

THE EARLY WORK OF JOSEPH HENRY.

By James F. McElroy.

Joseph Henry was born in Albany, December 17, 1797, and lived in this city the greater part of the time until 1832. It is true that the record in the old family Bible has left the date of his birth uncertain whether it occurred in 1797 or 1799, and his biographers have accepted the latter date as correct. However, this question is settled by other proof. The baptismal records of the First Presbyterian Church of Albany show that Joseph Henry was baptized January 21, 1798, and state that he was born December 17, 1797. This date can therefore be accepted as correct.

In 1826 Joseph Henry became instructor in mathematics in the Boys' Academy, of this city. If you go up State Street a couple of blocks, you will come to Capitol Park, in which our State Capitol is located. At your right you will then see a beautiful park, known as Academy Park, and in this park you will see the handsome brown-stone building of the Boys' Academy, which stands to-day just as it stood in the time of Joseph Henry. Joseph Henry continued as instructor in the Boys' Academy until the summer of 1832, and it was here that he made some of those great discoveries that have made his name imperishable in the annals of science.

In 1829 the highest development in electro-magnetism was represented by the old Sturgeon magnet. This magnet was made of a little round bar of iron, ¼ inch in diameter, which was bent into the shape of a horseshoe. It was then covered with varnish, to afford insulation for the winding. On the varnished surface was then wound 17 turns of bare copper wire, and these turns were spaced apart to prevent short-circuiting. The magnetic effects obtained with the Sturgeon magnet were very feeble.

In March, 1829, Prof. Henry read a paper before the Albany Institute (which occupied rooms on the second floor of the south end of the Boys' Academy Building), and in this paper he described improvements which he had made in the electromagnet, by which electromagnetic effects were obtained several hundred times as great as were ever obtained before. Prof. Henry's improvement consisted in first covering the wire with cotton or silk insulation and then winding the wire thus insulated into a close coil many layers deep around the iron bar. He also used a large bar of iron, many times as large as that used by Sturgeon. The result was that he obtained a magnet that would sustain over 2,000 pounds. In this way Joseph Henry produced the electromagnet as it is used to-day in various kinds of electrical apparatus in all countries of the civilized world.

If we examine a dynamo of any modern type, we will find large iron cores, which are surrounded by deep coils of insulated wire, containing many hundred turns of wire, which turns are kept from contact with each other by means of cotton or other insulation which is wound upon the wire before the coils are formed. In this coil the electric current is compelled to flow through the wire forming the coil many hundred times around the iron core. By this construction, the magnetic effects are increased to any desired amount. This is exactly the construction of the Henry magnet of 1829. All dynamos and motors depend upon this electromagnet of Joseph Henry for their operation, and no other means of exciting magnetism has since been discovered which can be employed, instead of the Henry magnet, to make dynamos and motors operative. This shows the fundamental character of Henry's contribution to the electric art. Joseph Henry thus placed in the hands of scientific investigators a new implement which made numerous discoveries in electrical science possible.

After the invention of the electromagnet and the discovery of the principles involved in producing electromagnetism, Joseph Henry constructed at Albany the first electromagnetic telegraph. In adapting the magnet for use on telegraph lines, Joseph Henry pointed out the necessity of winding the magnet with hundreds of turns of fine, insulated copper wire and using with this magnet, which he called his intensity magnet, a battery consisting of a

large number of cells connected in series. He constructed a telegraph apparatus in the Albany Academy, consisting of the intensity magnet and series battery and a long wire, which was supported on the walls of the large room in the academy. He used a suitable key for making and breaking contact and in front of the magnet was placed a movable armature, which was caused to strike against a sounding piece of metal and was so connected and arranged that by operating the key the action of the magnet upon the armature caused sound corresponding to the contacts made with the key. He further explained that the electromagnetic telegraph was now possible and that electromagnetic effects could be produced at almost any distance from the transmitting station. It will be clearly perceived that this apparatus contained the elements of the electromagnetic telegraph as it is in use to-day.

In 1833, after his removal from Albany to Princeton, he constructed a telegraph line supported upon insulators on poles and with the ends of the telegraph line connected to earth. He also connected to his telegraph line a local circuit containing a battery and low intensity magnet, which circuit was operated by means of a high intensity magnet placed in the main line. Thus, two other features of the modern telegraph were contributed by Joseph Henry, namely, the use of the earth as a return and the use of the relay circuit. This apparatus was shown at Princeton before his classes every year from 1833 to 1837. It did not contain what is known as the printer, which was afterwards invented by Prof. Morse. In the Morse printer, the magnet of Henry's relay circuit was caused to make depressions in a strip of paper which, by a clock movement, was caused to move over a point attached to the armature of the magnet. But the telegraph, as it is used to-day, does not use the Morse printer. It is simply a sounding apparatus as first proposed and constructed by Joseph Henry.

In the apparatus as applied by Morse to the telegraph line between Baltimore and Washington in 1844-45, and in all subsequent apparatus constructed by Prof. Morse, there was not only used the Henry electromagnet, but there was used the Henry intensity magnet in connection with the large number of cells connected in series. There was also used the relay circuit and the land line supported on poles on insulators, using the earth

return as first proposed and put in operation and explained by Joseph Henry. Henry's contribution to the electromagnetic telegraph was therefore fundamental and absolutely necessary to the operation of the telegraph, and without Henry's contribution the Morse apparatus could not possibly be made to work.

Another discovery was made by Joseph Henry at Albany prior to 1832, which has made his name famous wherever electrical science is known. It was here that Prof. Henry discovered the peculiar phenomenon known as self-induction, or the inductive effect which a long wire wound in a coil has upon itself. His discoveries in this line were extended to numerous discoveries in mutual induction or the inductive effect of one coil of wire upon a neighboring coil and to the way in which this effect was increased or decreased by the nearness of the second coil. He also discovered the effect of placing iron within the exciting coil. He also discovered that by placing a sheet of metal between the two coils the inductive effect could be cut off. He here laid down the principles which govern the construction of the induction coil and the alternating current transformer, both of which are used extensively to-day in many kinds of electrical apparatus. Henry's contribution to the subject of electric induction made his name famous wherever electrical science is known.

It is well known that in establishing the units of electrical effects, the names of eminent discoverers have been given to such units, for the reason that it was desirable to select names for the different units which would not be associated in the public mind with other meanings than the meaning given to the name by the definition of the particular unit. For this reason, the name of volt was given to the unit of electric pressure in honor of Volta, who invented the volta pile.

The name of ampere was given to the unit of rate of electric flow in honor of Ampère, who made numerous discoveries in electricity and magnetism in the early part of the last century.

The name ohm was given to the unit of electric resistance in honor of Ohm, who in 1827 explained the relation between quantity of current, electric pressure and resistance.

The name of coulomb was given to the unit of quantity of electricity in honor of Coulomb, who more than a hundred years ago invented the torsion balance.

The name of farad was given to the unit of electric charge in

honor of the great Faraday, who, in the early half of the last century, made numerous discoveries in electrical and electro-chemical science.

The name of henry was given to the unit of electric inductive effect in honor of Joseph Henry for his numerous discoveries in electric induction.

Prof. Henry is the only American philosopher who has thus been honored by the selection of his name by an international congress as the name of any one of the electric units. So that to-day the name of Henry is used in all civilized nations, speaking various languages, as the name of the unit of electric induction. This was the greatest honor ever conferred by an International Electric Congress upon an American scientist. This selection of the name of Henry has since been approved by the action of the governments in all civilized nations by proper legal enactment.

The lateness of the hour forbids that I should speak at length of the further discoveries of Joseph Henry whilst a resident of Albany. These discoveries were along the line of electric induction, the electric motor, and especially in connection with his discovery of magneto-electricity, which discovery has generally been credited to Michael Faraday, because Faraday was the first to publish his results. Before closing, however, I would like to speak a few words of an associate of Joseph Henry in his early work here in the city of Albany.

You have, with commendable wisdom, selected, as your headquarters, the modern-equipped hotel in which we are now meeting, known as the Hotel Ten Eyck. This hotel takes its name from one of our distinguished citizens, James Ten Eyck, a descendant of Philip Ten Eyck, who was an associate of Joseph Henry. Prof. Henry states that many of his experiments in Albany were performed jointly with Philip Ten Eyck and attributes to Philip Ten Eyck alone a series of experiments to determine the variation in the strength of a magnet by a change in what we now know as ampere-turns, and also to determine the point of magnetic saturation. I refer to this as it is undoubtedly the first tests that were ever made to obtain the data which is now worked into our modern curves of magnetization of iron. As a pioneer in this branch of work, the name of Philip Ten Eyck is deserving of recognition.

DISCUSSION.

Dr. H. S. Carhart: I am very greatly interested in these remarks about Joseph Henry. I am particularly interested in the early recollections of Joseph Henry, and I wish to simply impress upon this Society the fact that these discoveries were made not such a great while ago. I myself was born within 10 miles of this spot, in this county, and only fifteen years after these experiments of Joseph Henry were made, and I do not consider myself exactly an antique yet. (Laughter.)

I regard this experiment of transmitting current around the room of the Boys' Academy in Albany as the first transmission of power on record. I look on it in that light, rather than in the light of the telegraph. I think it was the first transmission of power, on a small scale, to be sure, but Joseph Henry showed us how to do it. He had to have high electromotive force, and that is what we are all aiming after yet. What I want to tell you about particularly is another matter. You all know that the word "henry" was adopted for the unit of inductance at the Chicago International Electrical Congress in 1893. There were one or two interesting incidents connected with that. I chanced to be a member of the Chamber of Delegates myself, and the incidents which I will relate to you fell within my personal experience. When it came to a choice of a name for the unit of inductance, Profesor Mascart, of Paris, rose and made a speech recounting the work that had been done and the names used previous to that date. One of the names proposed, the "secohm," had been used in England, and the other proposed, the "quadrant," had been used in France. Professor Mendenhall and myself recommended that the name "henry" should be used. When the time came for the adoption of the expression to cover the unit of inductance, Prof. Mascart proceeded historically to that point in his address, and then, very soberly and sedately said, "but out of deference to our friends of America, I propose that we adopt the name 'henry.'" It was done in the most graceful manner possible, and the proposition was seconded by one of the English delegates, and that settled it. You can imagine that the American delegates were delighted.

Then came the wording of the definition of the unit of induct-

ance. What is inductance? A committee was appointed and split in two parts. I remember Prof. Rowland was in one section, and Prof. Ferraris, of Italy, was a member of the committee. There were two definitions brought in. Neither was satisfactory to those who had the duty of framing the definitions. The definitions were reported to the Chamber of Delegates, and then, within two or three minutes after the two were reported, Prof. Ferraris, who spoke English with great difficulty and imperfectly, proposed, in English, the definition of the unit of inductance as we have it to-day. It came from a man who did not profess to speak English.

Mr. Carl Hering: I am glad to see that the work of Henry is being recognized, and that the record will be published. I remember talking about Henry with Werner Siemens, the so-called father of the dynamo, in 1891, when the name of Henry was first proposed for the unit. He remarked to me that Henry's work was not of much importance. Werner Siemens was perhaps the leading electrician in the early days of the present electrical era, and he did not seem to know what Henry had done. So I am glad that the value of Henry's work is now being brought to light.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., April 30, 1908; President C. F. Burgess in the Chair.

ROBERT HARE'S ELECTRIC FURNACE.

By Charles A. Doremus, M.D., Ph.D.

Incident to a discussion concerning an appropriate badge for the American Electrochemical Society, various emblems were suggested. Among others, Hare's early contribution to electrochemistry appealed to the writer as exceptionally appropriate.

Quite apart from this, it is well to call attention to the pioneer work in the chemistry of high temperatures done by our distinguished countryman, who in a very recent German treatise is referred to as a French chemist [1] and whose Memoir in the Annales de Chimie is ascribed to "Robert Harn Jun."

Professor Marston T. Bogert, in his presidential address before the American Chemical Society, at Chicago, January 1, 1908, makes the following statement:[2]

"The first organization devoted specifically to chemistry was the Chemical Society of Philadelphia, founded in 1792. This was probably the earliest chemical organization in the world, as it was born forty-nine years before the first European chemical society (Chemical Society of London, 1841). Priestley appears to have been one of its active members."

"The most important communication presented to the society was that announcing the discovery of the oxyhydrogen blow-pipe. It was made on December 10, 1801, by Robert Hare, Jr., then but twenty years old, who subsequently became Professor of Chemistry in the Medical School of the University of Pennsylvania."

Hare states that by the use of the oxyhydrogen blow-pipe which he devised in 1801, and an account of which he published in 1802, which account was republished in London and Paris, he was "enabled to fuse several of the pure earths which had pre-

[1] Vogel, J. H., N. Caro and A. Ludwig, Handbuch für Azetylen, Braunschweig, Vieweg & Sohn, 1904, p. 7.

[2] J. Am. Chem. Soc. Vol. XXX, 1908, p. 166.

viously been deemed infusible, and, likewise, not only to fuse, but to volatilize pure platinum.

Subsequently my friend, Professor Silliman, by a more extended use of the instrument, fused a great number of substances insusceptible of fusion by the common blow-pipe."[3]

The abstract in the Annales de Chimie,[4] specifies his having melted baryta, alumina, silica, lime, magnesia (the two latter with difficulty), and to have melted a weight of platinum equal to that of two pennies, to a spheroidal regulus. Hare was of the opinion, from the appearance of the charcoal, that he had boiled gold, silver and platinum by the aid of the oxyhydrogen jet. He also caused plumbago, which was thought to be an iron carbide, and a kind of coal which is found on the banks of the Lehigh, to burn when thus heated, though they were both considered incombustible in the ordinary sense.

"Latterly, by multiplying the jets and using great pressure, I have been enabled to fuse more than two pounds troy of platinum, into a malleable mass."[5]

In this connection a further quotation is pertinent. "Of Drummond's Lime Light, and of Daniell's and Maugham's Blow-pipe, so called erroneously:

"391. Much has been said in some of the British newspapers of the application in light-houses of the light reflected by lime, when subjected to the flame of the compound blow-pipe. This is treated as a new invention, although in my original Memoir, published in the year 1802, I spoke of the light so created as intolerable to the naked eye. A similar observation will be found in the description given by my friend, Professor Silliman, of the phenomenon in question. It follows that the English operator can only lay claim to *a new application* of a previous discovery."[6]

Having obtained these high temperatures by chemical means, it is not surprising that Hare turned his attention to the possibilities of electrical heating. He designated the effects as follows:[7]

[3] A Compendium of the Course of Chemical Instruction of the Medical Department of the University of Pennsylvania, by Robert Hare, M.D., 4th Ed., Philadelphia, 1840, p. 66.

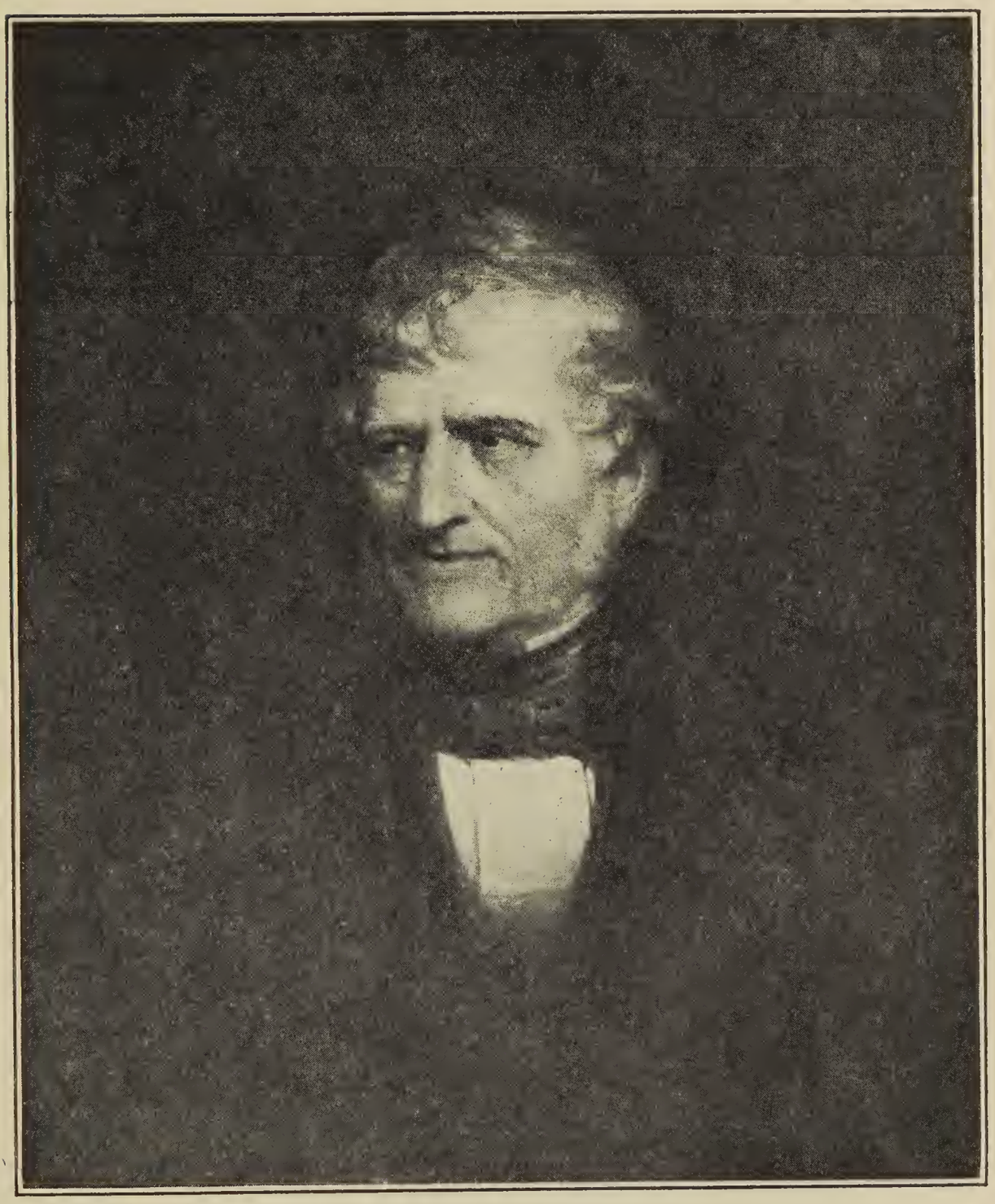
[4] Annales de Chimie, Tome XLV, p. 113, Paris, 1803.

Memoire sur l'usage du chalumeau, et les moyens de l'alimenter d'air, etc., par Robert Harn Jun. Plate, showing all details of construction.

[5] Hare's Compendium, p. 68.

[6] Hare's Compendium, p. 67.

[7] A Brief Exposition of the Science of Mechanical Eleetricity, or Electricity Proper, by Robert Hare, M.D., Philadelphia, 1840, p. 45.



ROBERT HARE.

"442. I deem it expedient to distinguish, under the general designation of continuous ignition, those cases in which a body to be ignited, is a good conductor (a wire or charcoal for instance), forming that part of the galvanic circuit which lies between the electrodes." He states that he heated several feet of platinum wire, and "446. If a prism of well-burned charcoal be made to connect the poles of a powerful deflagrator, on completing the circuit, by bringing the plates and acid into contact, the charcoal will be instantaneously ignited throughout."

"448. Those experiments in which the contact or continuity of the conductor between the electrodes, after being established, is destroyed by its reaction with the current, or by the interference of the operator, fall under the head of deflagration."[8]

He applied the principle of "ignition" to the explosive combustion of gaseous mixtures passing the current through a fine platinum wire. "In June, 1831, I was induced to make a series of experiments in order to explode the charges of gunpowder in rock-blasting, and succeeded by one of my deflagrators in exploding twelve charges at the distance of one hundred and fifty feet." This means was afterwards employed in England in blowing up the wreck of the "Royal George."[9]

In experimenting with the arc between charcoal points he obtained a light which he estimated as equal to 1600 candle-power. "The side of an adjacent house, on which the rays fell in the night, appeared as if illuminated by the sun." Both he and an assistant had badly inflamed eyes from injudicious looking at the light. He welded metallic electrodes together, even under water, and melted a platinum electrode of a quarter of an inch diameter instantly.[10]

For these and other electrical experiments, he constructed batteries of different types, calling some "calorimotors," others "deflagrators." The principle of plunging the plates into the acid, or causing the acid to flow upon all the plates simultaneously was adhered to in each.

In the large batteries, two troughs were joined lengthwise at

[8] Ibid., p. 47.
[9] Ibid., p. 47.
[10] Ibid., p. 48.

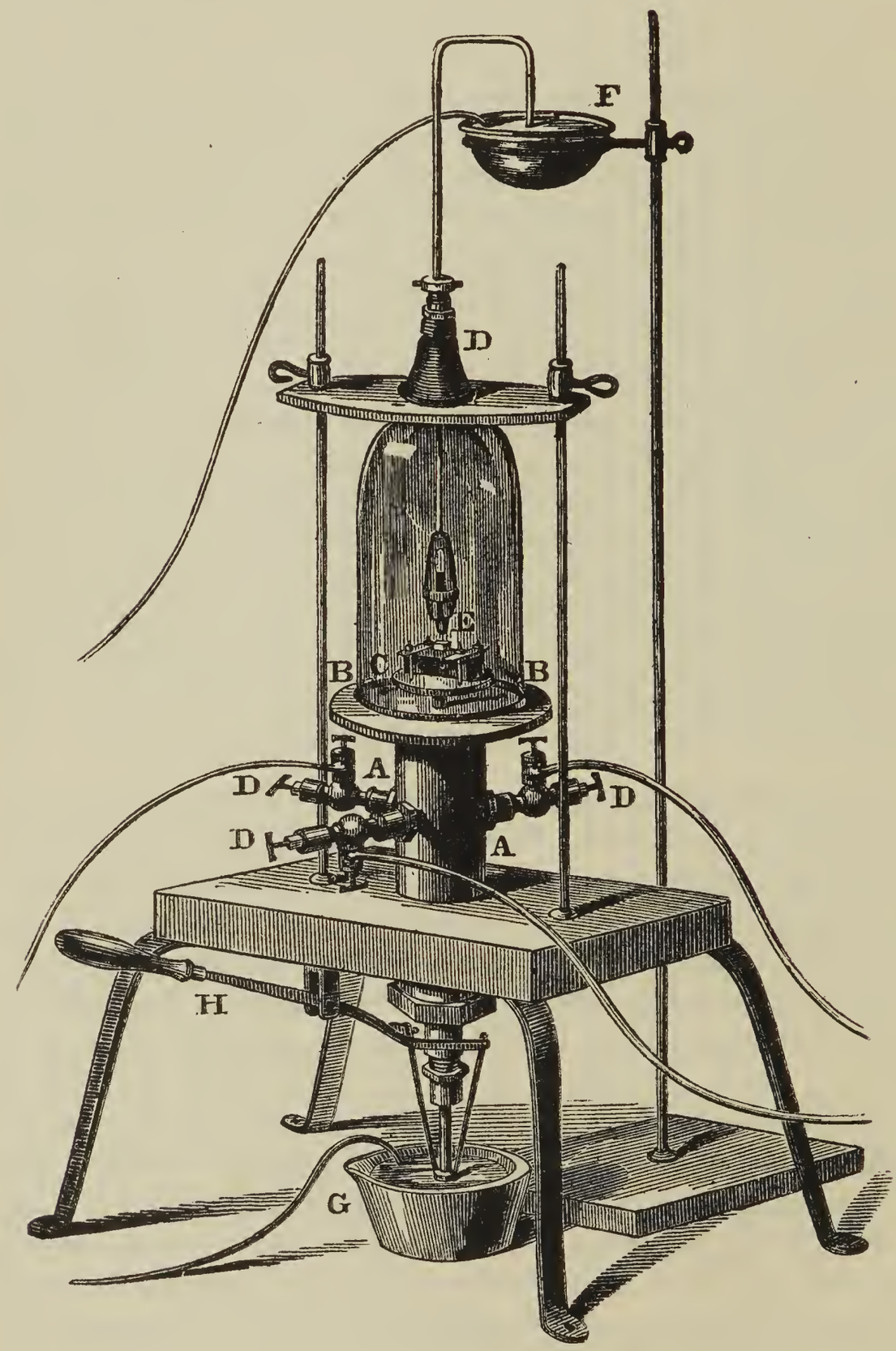
right angles to each other, both turning together on pivots placed at the ends. The dilute sulphuric acid in one trough could by a rotation of the battery of 90° be made to flow instantly upon all the copper and zinc plates, connected in series, which were fastened in the other. The effect of this sudden immersion is that, as corroborated by Faraday, "the great advantage is obtained of procuring for the experiment the effect of the first contact of the zinc and acid, which is twice or sometimes even thrice that which the battery can produce a minute or two after."

While powerful batteries had been constructed in Europe, notably that of Sir Humphry Davy, of 2,000 pairs, Hare is thus seen to have experimented on no small scale and to have been equipped with batteries suitable to operate the apparatus, which is the subject proper of this review. The original memoir appeared in the Transactions of the American Philosophical Society, held at Philadelphia, Vol. VII, New Series. Philadelphia, 1841, p. 53: Article V—"Description of an Apparatus for Deflagrating Carburets, Phosphurets, or Cyanides, in Vacuo or in an Atmosphere of Hydrogen, with an account of some Results obtained by these and other means; especially the Isolation of Calcium. By Robert Hare, M.D. Read October 18, 1839."

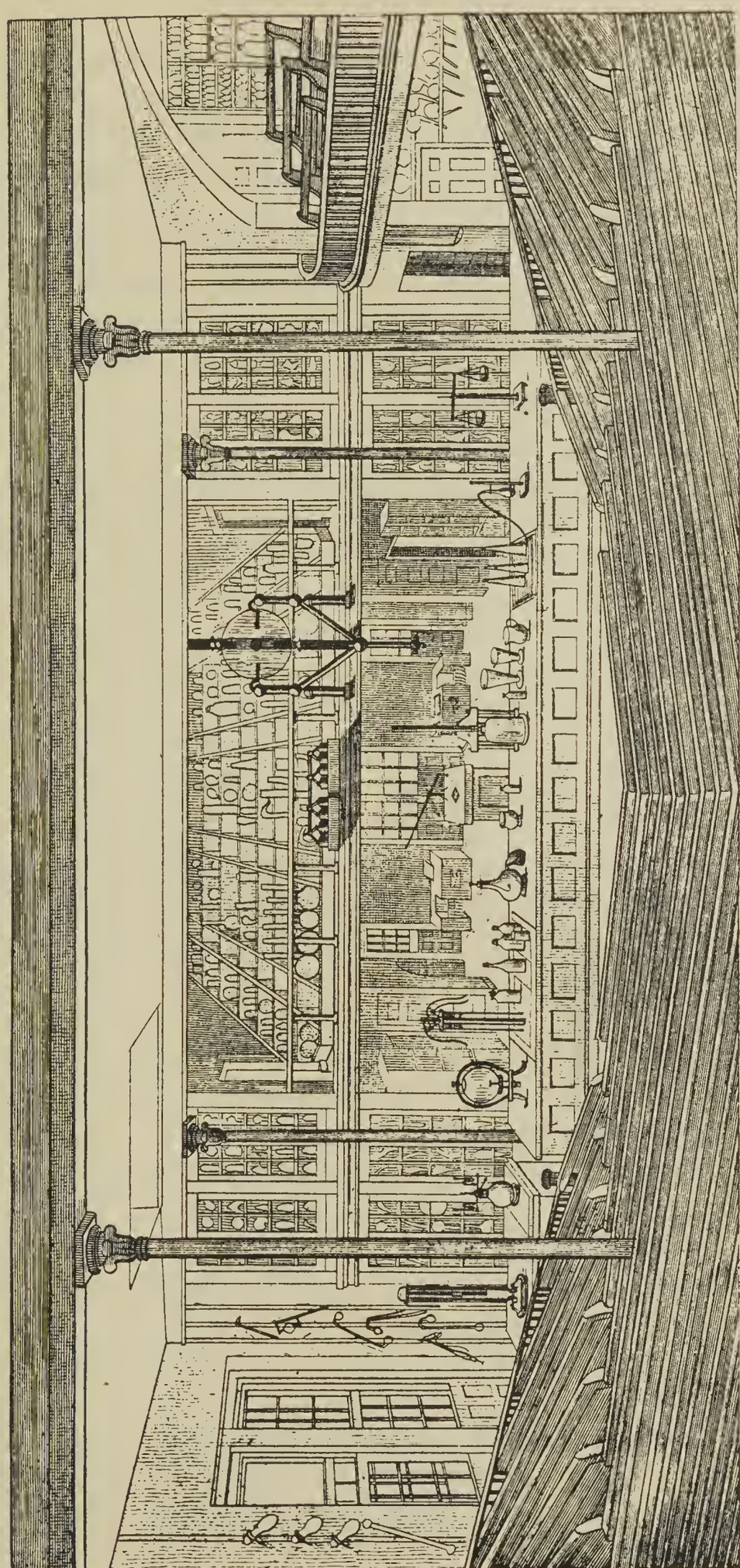
"Upon a hollow cylinder of brass (AA) an extra air-pump plate (BB) is supported. The cylinder is furnished with three valve cocks (DDD), and terminates at the bottom in a stuffing-box, through which a copper rod slides so as to reach above the level of the air-pump plate. The end of the rod supports a small horizontal platform of sheet brass, which receives four upright screws. These, by pressure on brass bars extending from one to the other, are competent to secure upon the platform a parallelopiped of charcoal. Upon the air-pump plate a glass bell is supported, and so fitted to it, by grinding, as to be air-tight. The otherwise open neck of the bell is closed air-tight by tying about it a caoutchouc bag, of which the lower part has been cut off, while into the neck a stuffing-box has been secured air-tight. Through the last-mentioned stuffing-box a second rod passes, terminating within the bell in a kind of forceps, for holding an inverted cone of charcoal, (E).

The upper end of this sliding rod is so recurved as to enter some mercury in a capsule, (F). By these means and the elas-

ticity of the caoutchouc bag, this rod has, to the requisite extent, perfect freedom of motion.



The lower rod descends into a capsule of mercury, (G), being, in consequence, capable of a vertical motion, without breaking



contact with the mercury. It is moved by the aid of a lever, (H), connected with it by a stirrup working upon pivots.

Of course, the capsules may be made to communicate severally with the poles of one or more deflagrators. The substance to be deflagrated is placed upon the charcoal forming the lower electrode, being afterwards covered by the bell, as represented in the figure. By means of the valve-cocks and leaden pipes a communication is made with a barometer gage (see fifth volume of this work); also with an air-pump, and with a large self-regulating reservoir of hydrogen.

The air being removed by the pump, a portion of hydrogen is admitted and then withdrawn. This is repeated, and then the bell glass, after as complete exhaustion as the performance of the pump will render practicable, is prepared for the process of deflagration in vacuo. But, if preferred, evidently hydrogen or any other gas may be introduced from any convenient source by a due communication through flexible leaden pipes and valve-cocks.

Having described the apparatus, I will give an account of some experiments made with its assistance, which, if they could have illuminated science as they did my lecture-room, would have immortalized the operator. But, alas, we may be dazzled, and almost blinded by the light produced by the hydro-oxygen blowpipe, or voltaic ignition, without being enabled to remove the darkness which hides the mysteries of nature from our intellectual vision.

I hope, nevertheless, that some of the results attained may not be unworthy of attention, and that as a new mode of employing the voltaic circuit, my apparatus and mode of manipulation will be interesting to chemists.

An equivalent of quicklime, made with great care from pure crystallized spar, was well mingled, by trituration, with an equivalent and a half of bicyanide of mercury, and was then enclosed within a covered porcelain crucible. The crucible was included within an iron alembic, such as has been described by me in this volume, as employed for the insolation of metallic radicals. (See page 38.)

The whole was exposed to heat approaching to redness. In two experiments the residual mass had such a weight as would result from the union of an equivalent of cyanogen with an equivalent of calcium.

A similar mixture being made, and in like manner, inclosed in the crucible and alembic, it was subjected to a white heat. The apparatus being refrigerated, the residual mass was transferred to a dry glass phial with a ground stopper.

A portion of the compound thus obtained and preserved was placed upon the parallelopiped of charcoal, which was made to form the cathode of two deflagrators of one hundred pairs, each of one hundred square inches of zinc surface, co-operating as one series.

In the next place, the cavity of the bell-glass was filled with hydrogen, by the process already described, and the cone of charcoal being so connected with the positive end of the series as to be prepared to perform the office of an anode, was brought into contact with the compound to be deflagrated. These arrangements being accomplished, and the circuit completed by throwing the acid upon the plates, the most intense ignition took place.

The compound proved to be an excellent conductor, and during its deflagration emitted a most beautiful purple light, which was too vivid for more than a transient endurance by an eye unprotected by deep-colored glasses. After the compound was adjudged to be sufficiently deflagrated, and time had been allowed for refrigeration, on lifting the receiver minute masses were found upon the coal, which had a metallic appearance, and which, when moistened, produced an effluvium, of which the smell was like that which had been observed to be generated by the silicuret of potassium.

Similar results had been attained by the deflagration, in a like manner, of a compound procured by passing cyanogen over quicklime, enclosed in a porcelain tube, heated to incandescence.*

Phosphuret of calcium, when carefully prepared, and, subsequently, well heated, was found to be an excellent conductor of the voltaic current evolved from the apparatus above mentioned. Hence, it was thought expedient to expose it in the circuit of the deflagrator, both in an atmosphere of hydrogen and in vacuo.

* After the above-mentioned experiments were made, I was led to believe that the compound, obtained as above described by heating lime with bicyanide of mercury, contained fulminic acid, or an analogous substance. The mass being dissolved in acetic acid, and the filtered solution subjected to nitrate of mercury, a copious white precipitate resulted. This being desiccated, proved to be a fulminating powder. It exploded, between a hammer and anvil, with the sharp sound of fulminating silver.

The volatilization of phosphorus was so copious as to coat nearly all the inner surface of the bell-glass with an opaque film in color resembling that of the oxide of phosphorus, generated by exposing this substance under hot water to a current of oxygen.†

The phosphuret at first contracted in bulk, and finally was, for the most part, volatilized. On the surface of the charcoal, adjoining the cavity in which the phosphuret had been deflagrated, there was a light pulverulent matter, which, thrown into water, effervesced, and, when rubbed upon a porcelain tile, appeared to contain metallic spangles, which were oxydized by the consequent exposure to atmospheric oxygen.

In one of my experiments with the apparatus above described, a portion of the carbon forming the anode appeared to have undergone complete fusion, and to have dropped in globules upon the cathode. When rubbed, these globules had the color and the lustre of plumbago, and, by friction on paper, left traces resembling those produced by that substance. They were susceptible of reaction neither with chloro-hydric nor with nitric acid, neither separately nor when mixed. They were not in the slightest degree magnetic.

About 1822, Professor Silliman obtained globules, which were at first considered as fused carbon, but were subsequently found to be deposition of that substance transferred from the electrode to the other. Several of these globules were, by him, sent to me for examination, of which none, agreeably to my recollection, appeared so much like products of fusion as those lately obtained.

Formerly plumbago was considered as a carburet of iron, but latterly, agreeably to the high authority of Berzelius, has been viewed as carbon holding iron in a state of mixture, not in that of chemical combination. It would not, then, be surprising if the globules which I obtained consisted of carbon converted from the state of charcoal into that of plumbago."

Hare further states:[11]

"454. There is no mode by which a small portion of a substance can be subjected to heat in the absence of the oxidizing

† The compound usually designated as the phosphuret of calcium consists, according to Thomson, of one atom of phosphate of lime, as well as two atoms of pure phosphuret. Hence, it is easy to see that the oxygen which enters into the constitution of the oxide, deposited, as above mentioned, upon the interior surface of the bell-glass, is derived from the phosphate.

[11] A Brief Exposition of the Science of Mechanical Electricity, p. 49.

influence of the air, or with the co-operation of the deoxidizing affinity of hydrogen so powerfully as that of a large voltaic series acting in a receiver capable of exhaustion and replenishment with that gas or any other. Subjecting phosphuret of lime in this way to the intense ignition produced by two hundred pairs, each of nearly seven and a half by fourteen (inches), I reduced the calcium very nearly to a state of purity, as a small portion acquired a metallic brilliancy under the burnisher, and decomposed water rapidly on being thrown into it.

"455. Having in like manner exposed cyanide of calcium, the result was similar, but less exceptionable, as this compound does not possess the property of liberating hydrogen from water, so that the acquisition of the property indicated more certainly that the substance evolved was calcium. In either case lime was found in the water, in which the supposed calcium had been immersed."

During the past year this apparatus was substantially reproduced under the supervision of Professor F. A. Holton, Washington, D. C., and was operated with a current from a "deflagrator" of 200 pairs, also reproduced, which developed a current of 125 volts and about 30 amperes.

A common blow-pipe charcoal 11 cm. long 3.2 cm. wide and 1.7 cm. thick, was used as the parallelopiped, and a charcoal pencil for the other electrode.

While the size of this *furnace* was not large, nor inferentially the original of Hare, since air-pump plates are rarely of large dimensions, its construction was *typical.*

Moissan's first furnace is thus described:

"In June, 1892, this electric furnace was made and worked at the École Supérieure de Pharmacie. It was fed with a current of 45 amperes at 40 volts, produced by a small dynamo. It was, therefore, a very modest apparatus made of two blocks of quicklime placed one above the other. A groove was cut in the lower block which allowed the two carbons of 8 to 10 m. m. diameter to pass. A small cavity was cut in the center of this block to hold a very diminutive crucible of gas carbon whose volume did not exceed two cubic centimeters. Nevertheless, he succeeded with this very simple arrangement in preparing, although in very small quantity, the greater number of the refractory metals. These first experiments sufficed for Henri Moissan to foresee the

advantage there was in introducing in the laboratory this new means of operating with the intense heat which the electric current can produce, and of making the electric arc a valuable auxiliary to the chemist."*

Though the apparatus of each is comparable in size, that of Moissan was, owing to the developments in Electrical Science and Art, operated with a current generated by a dynamo, which, if not more powerful, could be maintained indefinitely.

Hare obtained, despite the disadvantages of a current from a primary battery, calcium carbide, phosphorus, graphite, and metallic calcium, and there are just reasons, therefore, for regarding him as the earliest American scientific experimenter and discoverer in electrochemistry.

* Lebeau, Notice sur la vie et les travaux de Henri Moissan, Bull de la Société Chimique de France, 4e. Série. t. III IV, p. XIV, Paris, 1908.

A paper read by title at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 1, 1908; President C. F. Burgess in the Chair.

ON THE DIRECT SYNTHESIS OF HYDROCYANIC ACID.

By E. W. Smith, M.Sc. and R. S. Hutton, D.Sc.

Introduction.

The following is a brief account of an experimental investigation carried out in the early part of 1906. The successful results which were obtained clearly indicated the possibility of directly producing hydrocyanic acid and cyanides from carbon and gaseous mixtures, such as producer gas, containing nitrogen and hydrogen. The process was described in its essential particulars in a British patent, No. 23835, of October 26, 1906. Subsequently, H. Von Wartenberg published an account of a somewhat similar line of work,[1] but his interest appears to have centered around the thermodynamical calculation of the equilibrium, and the experiments described are not very extensive.

Whilst the present research clearly proves that hydrocyanic acid can be formed at much lower temperatures than were hitherto considered necessary, and thus indicates some promise of the process proving of practical utility, it must be admitted that the investigation is still in an incomplete state, the work having been interrupted by the departure of one of us from Manchester before the results could be exploited on a sufficiently large scale to obtain the data necessary for estimating the economic value of the process.

Resume of Previous Work.

The problem of the synthetical preparation of cyanides has attracted a considerable amount of attention, and it is impossible in a brief note to do credit to all the work which has been carried

[1] Zeitschrift für anorganische Chemie, **52**, 299-315 (1907).

[2] See { R. Robine and M. Lenglen, "L'Industrie des Cyanures," Paris: Béranger, 1903. W. Bertelsmann, "Technologie der Cyanverbindungen," Munich: Oldenbourg, 1906.

out.[2] The methods of attacking the problem may be divided into three classes.

(1). Action of nitrogen upon carbon at high temperatures *in presence of alkalies.*

(2). Gaseous reactions between nitrogen and hydrocarbons under influence of high tension electric arc.

(3). Direct synthesis from carbon, hydrogen and nitrogen at high temperatures.

It is the third class alone that it is necessary to consider here.

Along these lines, very little work appears to have been done, the reaction of nitrogen upon carbon apparently commencing at much higher temperatures than in the presence of the alkalies or alkali earths, and consequently being of less technical interest. The only previous investigation which has been discovered is that of Sir James Dewar. In two papers[3] he has given a full account of the experiments carried out with a view to synthesizing HCN.

In Dewar's first series of experiments, an electric arc was maintained between carbon electrodes in an enclosed space, through which air or hydrogen could be passed. The exit gases were passed through water, in which hydrocyanic acid was subsequently detected. By using hollow electrodes and withdrawing the gases through the + or — electrode, comparative experiments were made as to the relative amounts produced at the two poles. The inference drawn was that the high temperature of the + crater of the arc is essential for the reaction, which was ascribed as probably due to the reaction of acetylene with free nitrogen. In the second series of experiments, a carbon tube embedded horizontally in a limestone block formed the positive electrode; the arc being struck between this tube and a vertical solid carbon. The gases under examination were passed through the tube. Here again evidence of the formation of HCN was obtained, but the author appears to consider the high temperature of the arc essential for the reaction.

Experimental Work.

As it is of considerable interest to know if the direct synthesis of HCN can be carried out at lower temperatures and under

[3] Proc. Roy. Soc., **29**, 188-189 (1879).
Proc. Roy. Soc., **30**, 85-88 (1880).

conditions which preclude the intervention of any of the complicated electrical conditions which prevail in the arc, the authors

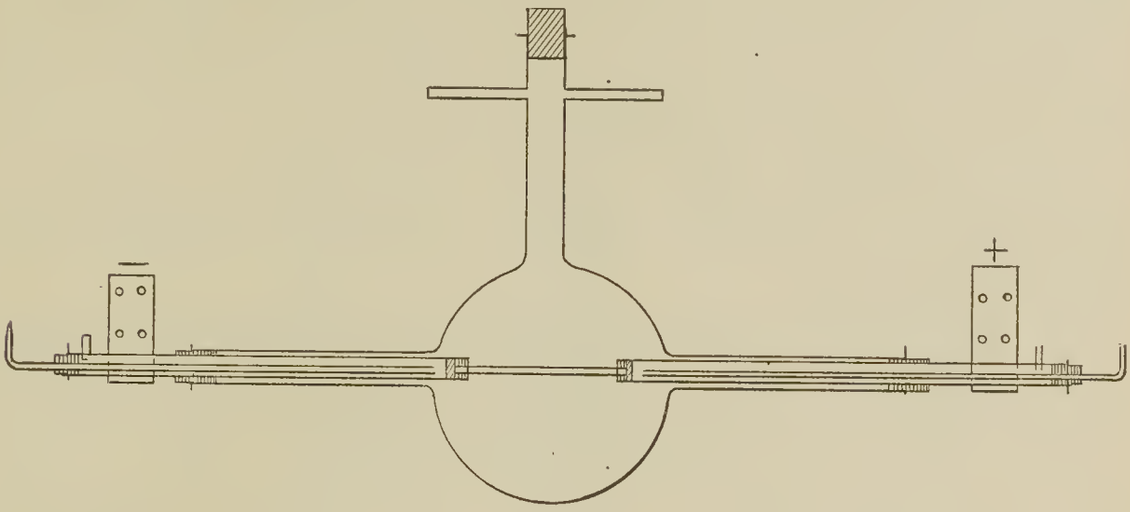


FIG. 1.

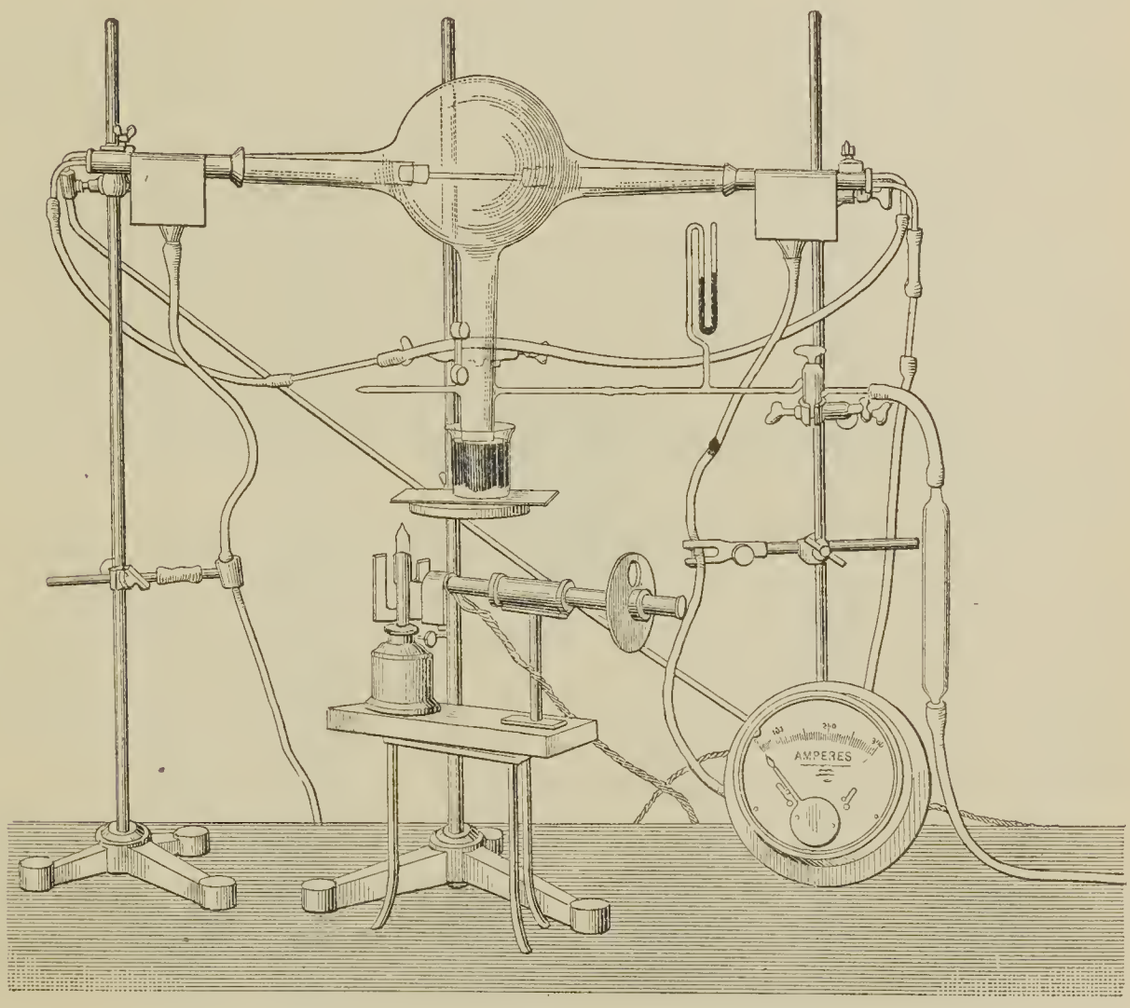


FIG. 2.

proceeded to study the reaction with an apparatus designed and employed in this laboratory for several other researches.[4]

[4]. See J. N. Pring and R. S. Hutton, Trans. Chem. Soc., London, 89, 1593 (1906).

In this apparatus (Figs. 1 and 2), a rod of carbon is heated by the resistance which it offers to the passage of an electric current, every precaution being taken to prevent arcing.

Water-cooled brass tubes serve to conduct the electric current to the carbon rods (of 3 to 6 mm. diameter), the ends of which are electro-coppered and soldered to the tubes.

The temperature, which can be regulated with delicacy by adjustment of the electric current, is estimated optically with a Wanner pyrometer.

The brass tubes are fixed air-tight into a tubulated glass flask of about 1.5 litres capacity, in such a manner that the heated rod is at a considerable distance from the glass walls. A slow current of gas is passed through the apparatus, the exit gases being allowed to bubble through a "Stromeyer" washer containing caustic soda solution (15 per cent.).

In all cases, the indication of hydrocyanic acid by the Prussian blue test was confirmed by an estimation of the quantity produced by titration with 0.1N silver nitrate solution.

In general, the experiments clearly prove that when carbon is maintained in contact with hydrogen and nitrogen below a temperature of some 1800° C., cyanide is not produced in noticeable quantity. This conclusion is borne out not only by the analysis and the absence of cyanides in the caustic potash used as absorbent, but also by the unaltered appearance of the carbon rod.

On the other hand, at all temperatures above about 1800° C. the reaction proceeds, HCN is produced, and the carbon rod shows evident signs of attack, disintegrating to quite a marked extent; moreover, the relative quantity of HCN formed rapidly increases with the temperature, experiments having been performed at different temperatures ranging up to 2500° C.

In the case of ammonia, the production of cyanide is, as might be expected, increased, but it is of some interest to note that the temperature at which the reaction occurs is not to any marked extent lower than with nitrogen and hydrogen.

Finally, the production of cyanides from mixtures of gases containing CO, such as correspond to producer gas, has been shown to proceed satisfactorily, and particularly in this latter case the process is of practical value, on account of the difficulty and expense of preparing pure nitrogen.

The foregoing experiments, some typical examples of which are given as an appendix to the paper, are obviously of a laboratory type, suited more particularly for determining with

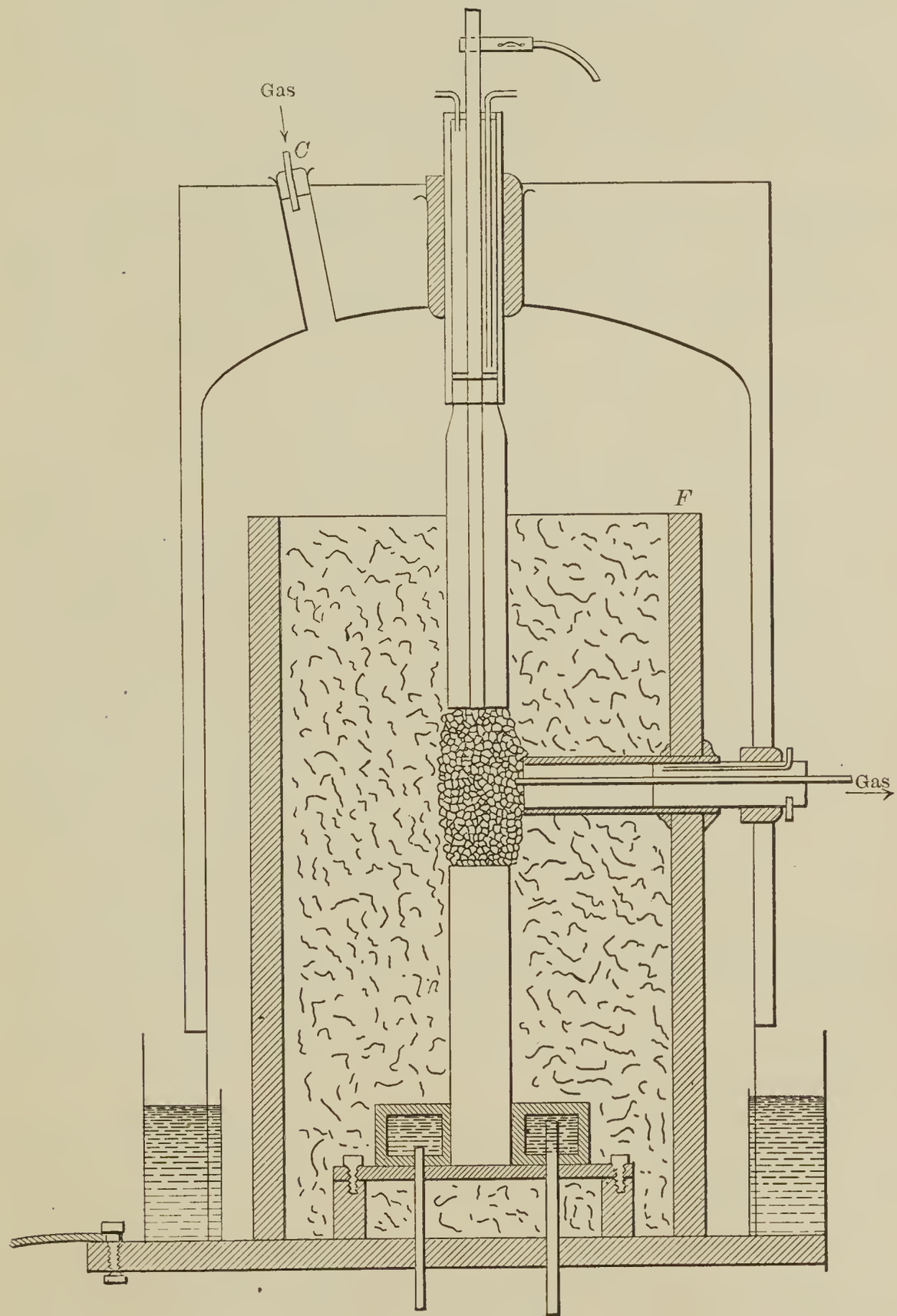


FIG. 3. Scale one-fifth.

some exactitude the temperature conditions and the effect of different gas mixtures upon the course of reactions.

As a step towards the application of these results to larger scale working, an apparatus was devised as illustrated in Fig. 3.

The principle here adopted is to bring the gaseous mixture (nitrogen and hydrogen, together with carbon monoxide) in contact with highly heated carbon, means being provided for rapidly withdrawing the gases from the high temperature zone, so that they could be cooled sufficiently rapidly to preclude the decomposition of HCN, formed in the region of high temperature.

Further, an attempt was made to obviate the somewhat wasteful expenditure of energy which is necessarily incurred when the highly heated zone is surrounded on all sides with a free gas space, with the accompanying loss of heat by powerful convection currents.

In the arrangement illustrated, the gases gradually reach the zone of high temperature by percolating through the layers of the charge, retort carbon (in practice, coke or other suitable material might be used), and thus are economically preheated; only the gas which has actually passed through the region of maximum temperature is suddenly cooled by direct withdrawal.

The form of apparatus shown in the sketch has two carbon electrodes, with a surrounding charge of ground carbon; the portion of the charge between the two electrodes is heated to a high temperature by the resistance which it offers to the passage of the current. One of the electrodes is provided with a central channel through its axis for the removal of the gas.

In a modified type of furnace which was also tried, the two electrodes are solid, whereas a horizontal water-cooled tube projects from the outside of the furnace into the central zone between the two electrodes, this water-cooled tube serving to withdraw the gases by suction or by the positive pressure which prevails inside the vessel.

A fireclay cylinder, F, serves to retain the charge of carbon in place, and a large water-cooled iron bell, with water seal, renders the whole chamber gas-tight.

The apparatus is connected at C with a gasometer (10 cubic feet capacity), into which the gases were conducted from their respective generators. Hydrogen and nitrogen were prepared

separately in generators of the type described previously,[5] the relative quantities of the gases in the mixture being adjusted and easily regulated by the simple device also described in this paper on gas preparation.

Owing to the difficulties of making lengthy runs of this kind in a laboratory and to the impossibility of continuing these experiments, the cause of which has been previously referred to, this series of experiments was confined to a demonstration of the possibility of producing hydrocyanic acid under conditions such as are described.

It is hoped that an opportunity may be found for continuing and extending the research, and it may be confidently expected that trials on a larger scale and with more ample resources would yield results of considerable value to the important question of nitrogen fixation.

The chief result of the work is obviously the definite proof of the formation of HCN at temperatures very far below those of the electric arc and under conditions which almost certainly preclude the intervention of complicated electrical effects such as are characteristic of the arc. It appears, also, that the formation of cyanides by interaction of carbon and nitrogen in presence of alkalies and alkaline earth oxides may be largely accounted for by the direct production of hydrocyanic acid and its subsequent combination with the alkali, rather than of the complicated reactions which are generally supposed to account for the production of cyanides in these cases.

Electrochemical Laboratory, The University,
Manchester, England,
April, 1908.

[5] "The Preparation and Compression of Pure Gases for Experimental Work," by J. E. Petavel and R. S. Hutton, Journ. Society of Chemical Industry, **23**, 87-93 (1904).

APPENDIX.

Records of a Few Typical Experiments.

Experiment I.—The whole apparatus was well washed out with hydrogen and the exit gases tested for any trace of oxygen which might be present, the current of gas being continued until the air had been completely displaced and no trace of oxygen could be detected in a measured quantity of the gas. A mixture of N^2 and H^2 was then passed through the apparatus, the N^2 being in excess of the hydrogen.

Time.	Volts. (Across furnace terminals.)	Temp. (By Wanner Pyr.)	Current. (amperes.)
12.20	10	1,750° C.	140
12.30	10	1,787° C.	150

After this ten-minute run, the temperature of the rod was increased by raising the current, and the exit gases were passed through a fresh quantity of KOH.

		Current.
12.35	about 2,000° C.	195
12.45	about 2,000° C.	200

16 per cent KOH used.

Diameter of carbon rod before using.....6.03 mm.
Diameter of carbon rod after using.....5.63 mm.
Length of rod exposed.....7.5 cms.

Both solutions were tested by the Prussian blue test and showed marked signs of the presence of KCN, the second at the higher temperature, but same flow of gas, evidently containing a considerably larger quantity. Only a qualitative analysis was made in this instance.

Experiment II.—The heating of the rod in an atmosphere of *ammonia.* The ammonia was prepared from lime and NH_4Cl. The oxygen was again washed out, by means of H^2, and a strong current of ammonia run through.

Two experiments were made at different temperatures, but with the same flow of gas. The carbon rod in this case was shorter than previously.

	Time.	Amps.	Temp.
(1).	2.15	50	
	2.17	80	
	2.19	100	
	2.20	120	
	2.21	140	1,700° C.
15 mts.	2.30	140	1,750° C.

The current was here cut off, new 16 per cent. KOH put in, and a higher temperature attained.

	Time.	Amps.	Temp.
(2).	2.45	80	
	2.45½	100	
	2.46	120	
	2.46½	140	
	2.47	160	
	2.48	160	
	2.50	160	1,935° C.
	2.52	160	
8 mts.	2.53	160	

Titrations.—1.6 c.c., 0.1N, $AgNO_3$ = 10 c.c. of Sol made up to a litre.

(1). But 1 c.c. $AgNO_3$, 0.1N = 0.01302 gms. KCN.

∴ 160 $AgNO_3$, 0.1N = 2.0832 gms. KCN.

(2). 1 c.c. 0.1N, $AgNO_3$ = 10 c.c. Sol. previously made up to 1 litre

= 0.01302 gms. KCN.

∴ 1,000 c.c. = 1.302 gms. KCN.

As a check, the KOH solution was tested by titration with $AgNO_3$, but no trace of cyanide was detected, an immediate precipitate being obtained.

The $AgNO_3$ was also standardized by titrating against a known quantity of KCN. It proved to be 0.1N.

Experiment III.—The heating of the carbon in a mixture of CO, H^2 and N^2, with a percentage composition of 26 per cent. H^2, 34 per cent. N^2, and 40 per cent. CO.

One experiment only was made at a high temperature.

Time.	Current. (amperes.)	Volts.	Temp.
1.56	40		
.56½	70	5.1	
.57	90	5.8	
.58	120	7.3	
2.0	160	8.9	1,895° C.
.1	180	9.5	1,895° C.
.3	180	9.2	1,975° C.
.5	180	9.3	1,915° C.
.8	190	9.3	
.11	Stop		

The solution was made up to 100 c.c.

$$.7 \text{ c.c. } AgNO_3 = 10 \text{ c.c. of solution}$$
$$\therefore 100 = 7 \text{ c.c.}$$
$$= 0.08114 \text{ gms. KCN.}$$

The solution also gave the Prussian blue test.

Experiment IV.—A mixture of N^2 and H^2 was made, and analyzed

51.5 per cent. N^2,
48.5 per cent. H^2. No oxygen present.

After running the gases through the apparatus for some time, and having tested the exit gases for oxygen and finding none, the current was put on.

Time.	Current. (amperes.)	Furnace Volt	Temp.
10.25	25		
.27	70		
.28	100	6	
.29	130	7.5	
.30	150	8	
.35	160	8	1,800° C.
.36	180	9.3	1,860° C.
.38	185	9.3	
.41	187	9.9	1,860° C.
.45			

The KOH solution was then changed and a higher current used.

.46	200	12.7	2,088° C.
.47			

The carbon broke and arced. Cut off, and gases washed out.

Analyses. (1) 0.1302 gms. of KCN formed.
(2) 0.13624 " " " " (carbon kept).

Experiment V.—Apparatus similar to previous experiments. First experiment, but with carbons 5 mm. in diameter, 0.2 per cent. ash.

A mixture of gases (H^2 and N^2), in the proportion of 47 per cent. H^2 and 53 per cent. N^2, was passed directly through H_2SO_4 and into the apparatus.

No trace of oxygen was found to be present. After allowing the gases to flow through the apparatus for some time, the current was switched on and the following observations taken:

Time.	Amps.	Temp.
10.45	15	
.46	50	
.47	70	1,682° C.
.48	81	1,785° C.
.49	90	
.50	100	1,900° C.
.53	100	1,935° C.
.55	112	1,997° C.
11.00	130	1,997° C.
.03	140	2,105° C.

The apparatus was dirty, and in consequence, together with inaccuracies of reading caused by the glare of the light, the readings of temperature are not likely to be very accurate.

Titrations.—10 c.c. of solution (made up to 100 c.c.) = 1.6 c.c. 0.1N, $AgNO_3$.

$\therefore$ 100 c.c. = 16 c.c. = 0.01302 $\times$ 16 = 0.20832 gms. KCN.

A paper read by title at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., April 30, 1908; President C. F. Burgess in the Chair.

DISTILLATION OF TURPENTINE BY ELECTRICITY.

By F. T. Snyder.

Pine woods contain a series of volatile hydro-carbons having boiling points varying from 130° C. to 250° C. A mixture of these, including the groups which boil between 155° C. and 170° C., forms what is commercially known as turpentine. The principal constituent of this turpentine is pinene, with a boiling point of 155° C. to 156° C. The process of obtaining turpentine from wood by distillation is an extractive one, in that the turpentine exists in the wood substantially in the form in which it is obtained, and is not a product of decomposition at the time of extraction. At 175° C., the pinene of the turpentine begins to break up into a mixture of lighter and heavier hydro-carbons, the decomposition being substantially complete at 270° C. It is therefore necessary to distill turpentine within relatively narrow temperature limits. If the wood from which the turpentine is distilled is not heated enough, part of the turpentine will be left in the wood. If it is heated too hot, part of the turpentine produced will be destroyed. Many of the products formed in breaking up turpentine have strong odors, and a small percentage materially affects the selling price of the turpentine produced, as the smell nauseates the painter using the turpentine. It requires a certain drop of temperature to cause the heat needed to flow from the exterior to the center of a turpentine retort, and this further reduces the narrow range of temperature available.

It has been known for many years that the fir wood of the North Pacific Coast contains a considerable quantity of turpentine, and efforts had been made to utilize it as a basis for the commercial production of turpentine. The principal difficulties encountered were those inherent in the close regulation of

temperature necessary. Some years ago, the obvious possibility of close temperature regulation obtainable with heat from electricity suggested the use of heat from electricity in the distillation of turpentine from this fir wood. At Vancouver, British Columbia, a considerable supply of waste fir wood was available, in the form of saw-mill refuse, and electricity from water-power was available at a low cost. An experimental electric turpentine plant, with a capacity of 1/16 of a cord, was erected and tested, and subsequently reported upon by Dr. T. H.

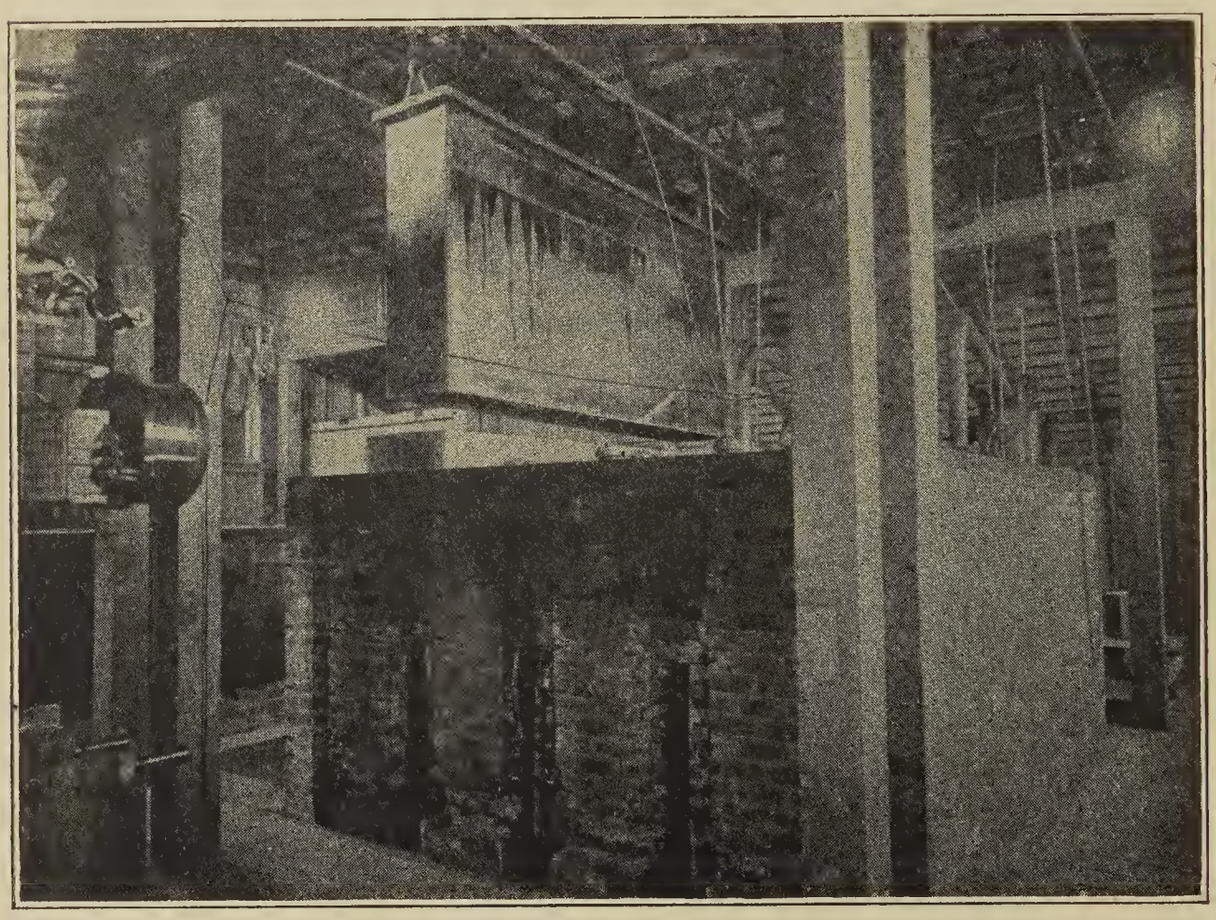


Fig. 1.

Bray, of the Massachusetts Institute of Technology. As a result of Dr. Bray's report, a commercial plant, with a capacity of three cords per day, was erected, and has been in operation at Vancouver since July, 1907.

The wood supply for this plant is brought in by barge, from neighboring saw-mills, and landed at a dock adjoining the plant. On this dock the wood is filled into cans, which are wheeled into the plant, picked up by an overhead crane (Photograph 1), and dropped into a brick retort, forming one of a

group which are placed together to reduce radiation. The top of the can forms a flange, which dips into a groove around the top of the retort, filled with tar, forming a gas seal when the can is in the retort. Electricity at 110 volts is carried through wrought-iron strips threaded through the brickwork on each side of each retort. The current supply for each retort is controlled by a switchboard of ordinary type, which also holds the direct reading pyrometers, one of which registers the temperature at the outside of the can and one the temperature

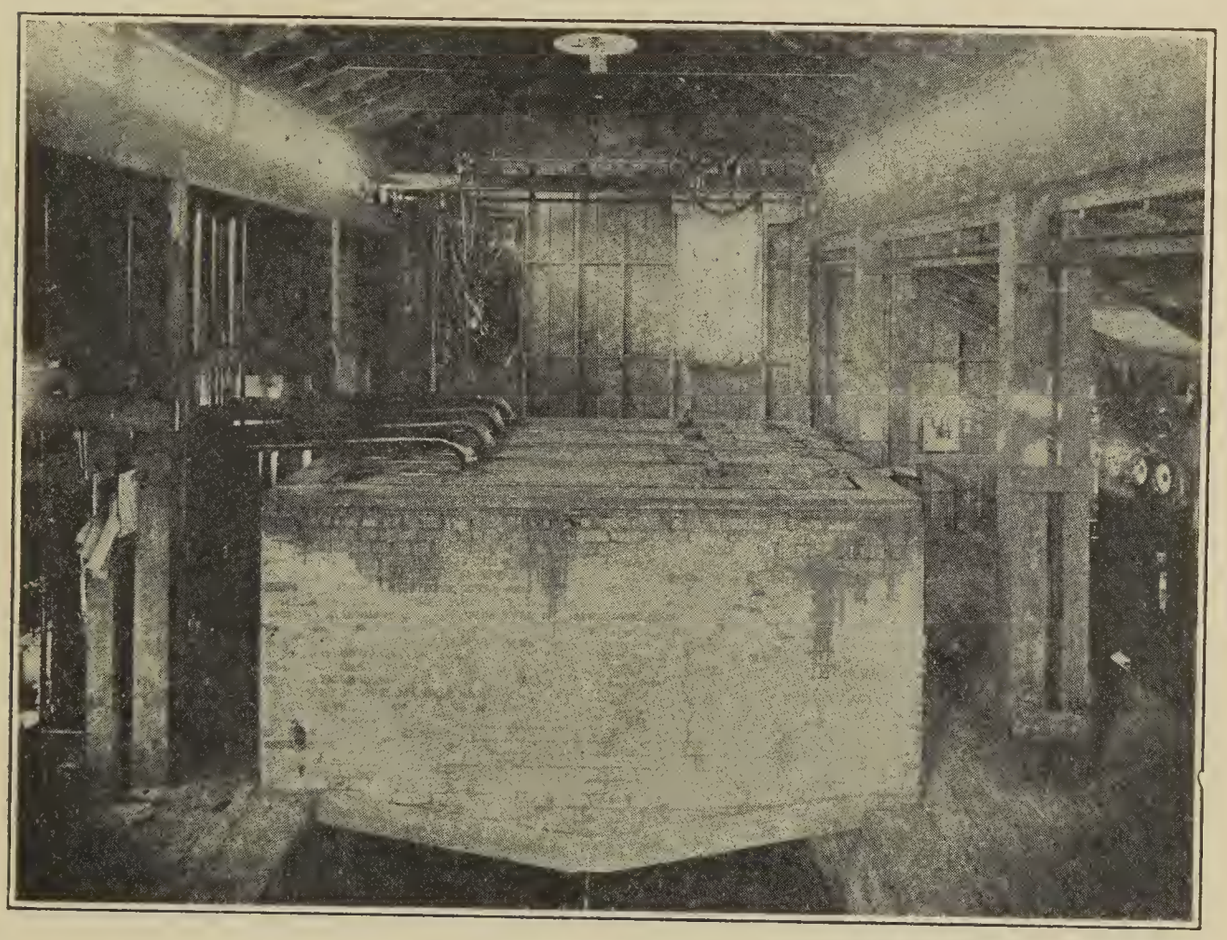


FIG. 2.

at the center of the can, showing the maximum and minimum temperature conditions in the can. The leads of these pyrometers end in flexible extensions on the top of the retorts which can be changed from can to can (Photograph 2). The turpentine vapor is taken from the retort through a removable copper outlet pipe. This outlet pipe leads to a condenser (Photograph 3), which consists of an upright copper pipe, down which a spray of water is passed through the ascending turpentine vapor, and which terminates in a tank at the bottom. The tank serves as

a separator for the condensed turpentine and water, the turpentine readily floating to the top of the water. The excess water from the spray is withdrawn from the bottom of the tank, and the turpentine taken off from the top of the tank into a storage system.

The brickwork of the retort, when a can newly filled with wood is put in it, is about 250° C. The cold can rapidly absorbs heat from this brickwork, the temperature of the brickwork being kept up by a current of 400 amperes, which is put through

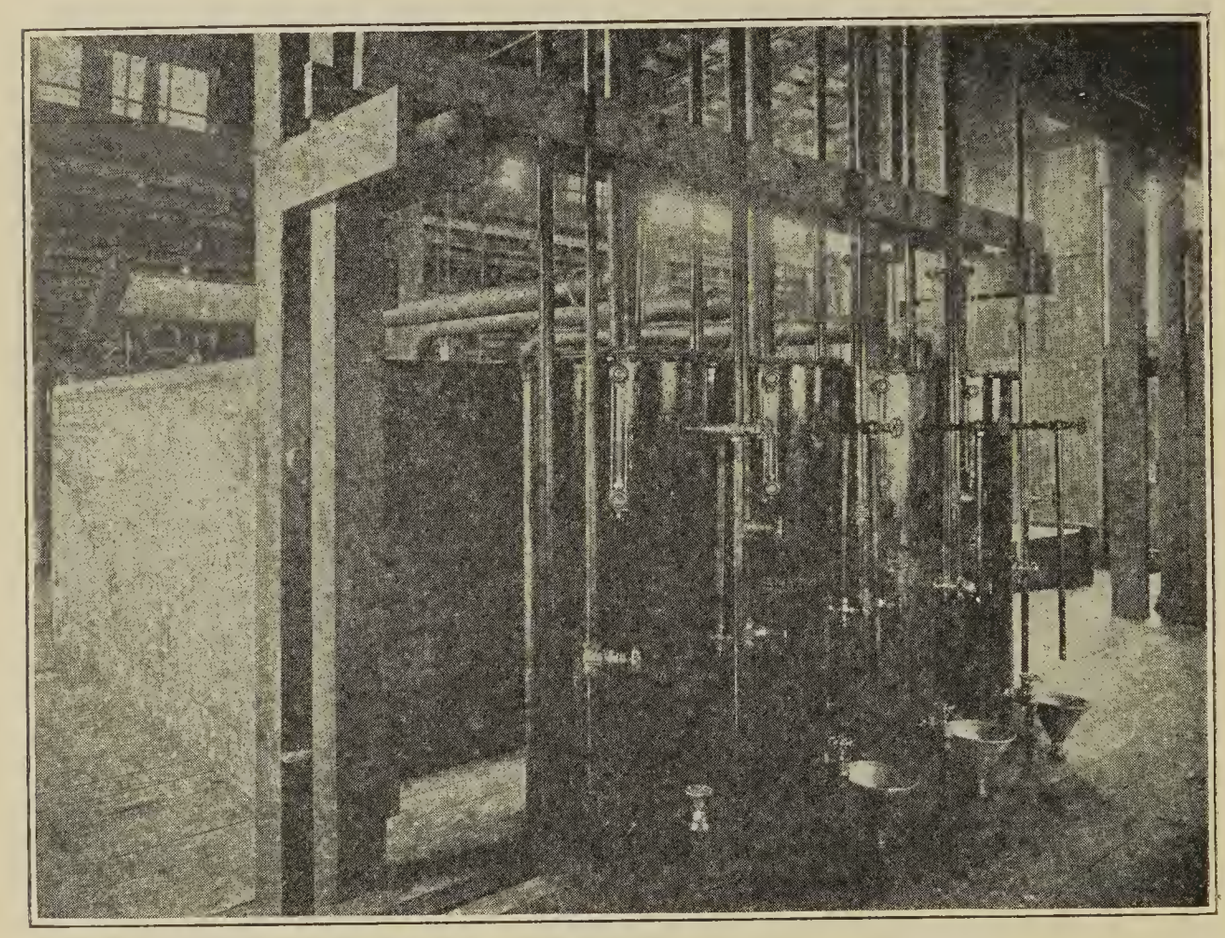


Fig. 3.

the resistance strips for about two hours. During this time, the temperature at the outside of the can rises from 75° to 130° C., at which turpentine begins to come off and at which time the center of the can is at 45° C. The current is then shut off, and the temperature of the can slowly rises by absorption of heat from the brickwork for two hours longer, when the temperature has reached 150° C. on the outside of the can and 205° C. in the center of the can and the turpentine has been substantially all removed. In practice, it is found that from

90 to 95 per cent. of the turpentine in the wood, as determined by analysis, is removed during this interval. While the turpentine is coming off, the pitch in the wood melts and runs down to the bottom of the can and out through perforations, and is collected in the bottom of the retort, from which it is drawn off, at the end of the run, into the barrels in which it is shipped.

It will be noted that the temperature of the interior of the can at the end of the turpentine run is hotter than the outside. This is due to the heat which is beginning to be liberated by the decomposition of the hydro-carbons in the wood. At this point the can is lifted by the overhead crane from the turpentine retort and put into the adjoining retort, a new can of raw wood taking its place in the turpentine retort. In its new position, the original can of wood, from which the turpentine has been extracted, is connected up by another copper outlet pipe to the adjacent condenser. This change of retort and piping keeps the turpentine condenser and piping from being fouled by tar oil or tar products. Due to the continued decomposition of the wood, the temperature steadily rises without further use of electricity, and the resulting decomposition gives a product known commercially as "tar oil" and which comes off as vapor and is condensed. The other product of this decomposition is wood tar, which trickles down as the rosin did in the turpentine retort and is collected in the bottom of the tar retort. It is found in practice that this tar tends to break up at the final temperature of the tar retort, and it is consequently drawn off continuously, during the tar run, into the barrels in which it is to be shipped. At the end of three hours of the tar run, the temperature in the center of the can has risen to 375° C. and tar oil and tar stop coming off. The can is then lifted out and stood on a sand floor, which makes an air seal with the lower edges of the can and protects from combustion the contents of the can, which now consists of charcoal. When the can and its charcoal contents are cool, which takes about three hours, the perforated bottom of the can is tripped and the can lifted, allowing the charcoal to fall out. This charcoal is then put in sacks, as required by the trade which consumes it.

Five products are produced from the wood, turpentine and

rosin in the turpentine retort, tar oil and tar in the tar retort, and a residual product of charcoal. The amount and kinds of product derived from any supply of wood depend on the character of the wood. The following will indicate the results which are being secured from the British Columbia Coast fir per 1,000 pounds of wood:

Turpentine	6.7	gallons
Rosin	168	pounds
Tar oil	5.1	gallons
Tar	68	pounds
Charcoal	323	pounds

It may be noted that this charcoal, being retort charcoal and cooled out of contact with air, is tough and suitable for special purposes. The amount of wood held by a can varies with the quality of the wood, but averages at Vancouver about 1,000 pounds. The electricity used per can is about 90 kilowatt hours and costs, at Vancouver, 18 cents per can of wood.

The plant is operated by one man on each shift, there being two twelve-hour shifts per day. When the wood is large, an extra man is employed on the day shift to split it.

Chicago, Ill.
March 10, 1908.

A paper read in abstract by Jos. W. Richards at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 1, 1908; President C. F. Burgess in the Chair

POWER FOR ELECTROCHEMICAL INDUSTRIES.

By John Meyer.

Electrochemical applications have so increased and the attitude of the central station has become so favorably inclined towards this class of business that undoubtedly the industry would be stimulated if there was a clearer understanding between the two interests.

As indicated in Mr. E. A. Sperry's paper, and the discussion of this paper at the Ninth General Meeting, and also in the paper read by the author at the Eleventh General Meeting, there are certain conditions which the central station must weigh in making rates.

These conditions have been very ably explained by Mr. C. J. Russell, in a recent paper read before the Association of Edison Illuminating Companies, and published by several technical journals, but which bears repetition.

"Considerable discussion has taken place as to the desirability of this class of business to fill in the hours between peaks, and thus to equalize the station load. In these discussions, great importance has been attached to the alleged fact that such business need not cross the peak and could be supplied with large or small volumes of current, according to the capacity of generators in service and the amount of other load upon the system at a given time.

"There is no question that such a class of business would enable a station to operate under ideal conditions. It is evident that the question, however, must be dealt with according to the exact conditions of capacity and load of each individual station contemplating such supply. General statements may lead to a serious misconception of the true possibilites in this direction.

"The character of load diagrams of all central stations which have cultivated the electric power field have undergone a radical change. In such cases, the old condition of morning and evening peaks which represented almost the total generated load has passed. In the present load diagrams, the kilowatt area of such peaks as exist must bear a much smaller ratio to the area of the daylight load.

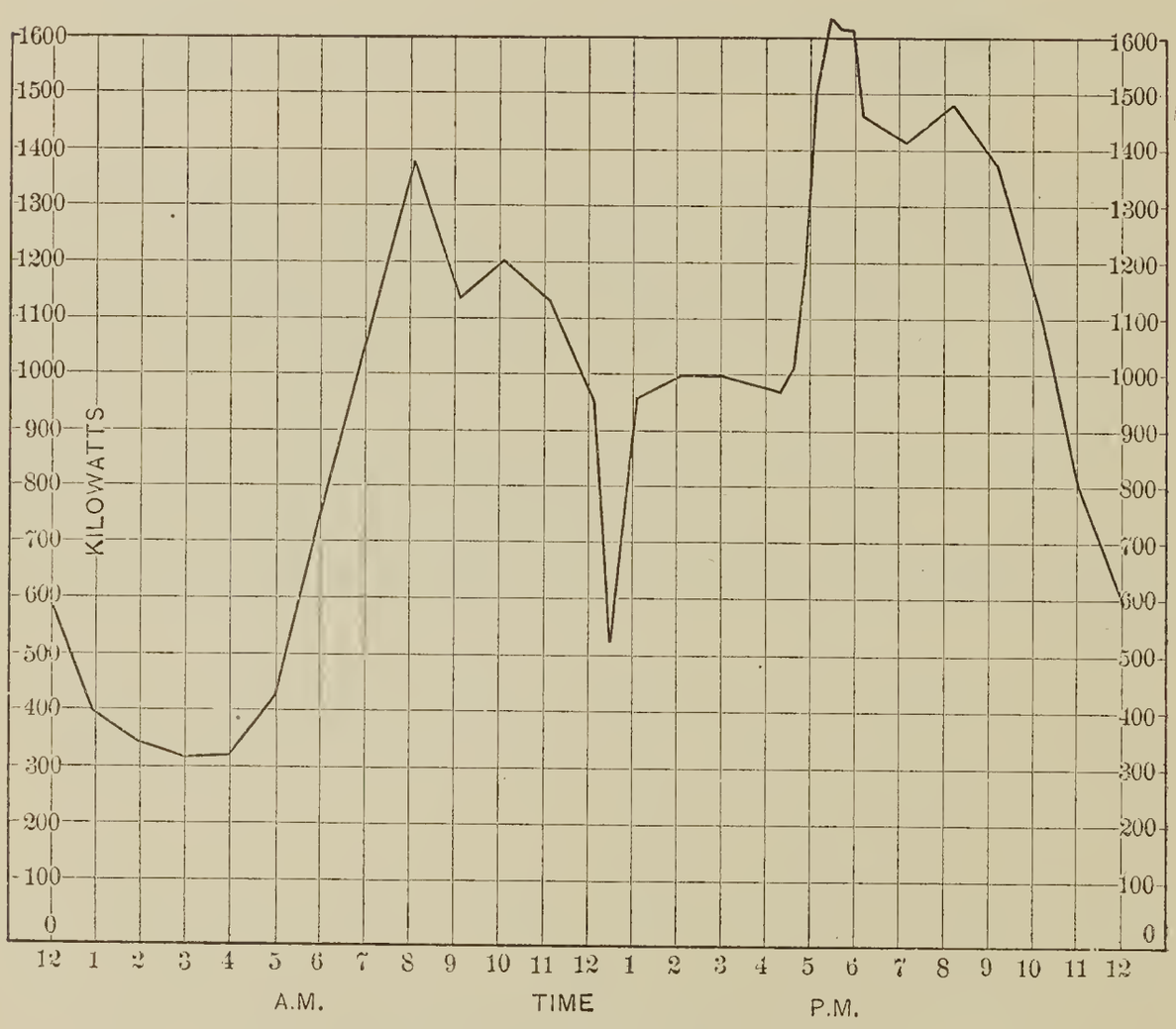


FIG. 1. Current Generated Dec. 15, 1905.

"An examination of some mixed load diagrams may help to draw some conclusions in this matter.

'Fig. 1 shows a load diagram of a small generating station on the highest day of 1905.

"Fig. 2 shows the load diagram of the same station on a day close to the shortest of the present year.

"In the case of the first diagram, the total kilowatt area was 23,540. In order to equalize the load to the maximum of 1,643 k.w. capacity, it would be necessary to utilize in the twenty-four

hours 15,892 k.w. hours, and the time and rate at which this was available is shown in Fig. 3.

"In the case of the shortest day, the total kilowatt output is 19,040, and in order to attain the maximum use of 1,643 k.w. capacity, we should have available a supply of 20,392 k.w. hours. The time and rate at which this was available is shown in Fig. 4.

"An examination of Figs. 3 and 4 will show that an electrothermic or electrochemical process must be capable of wide

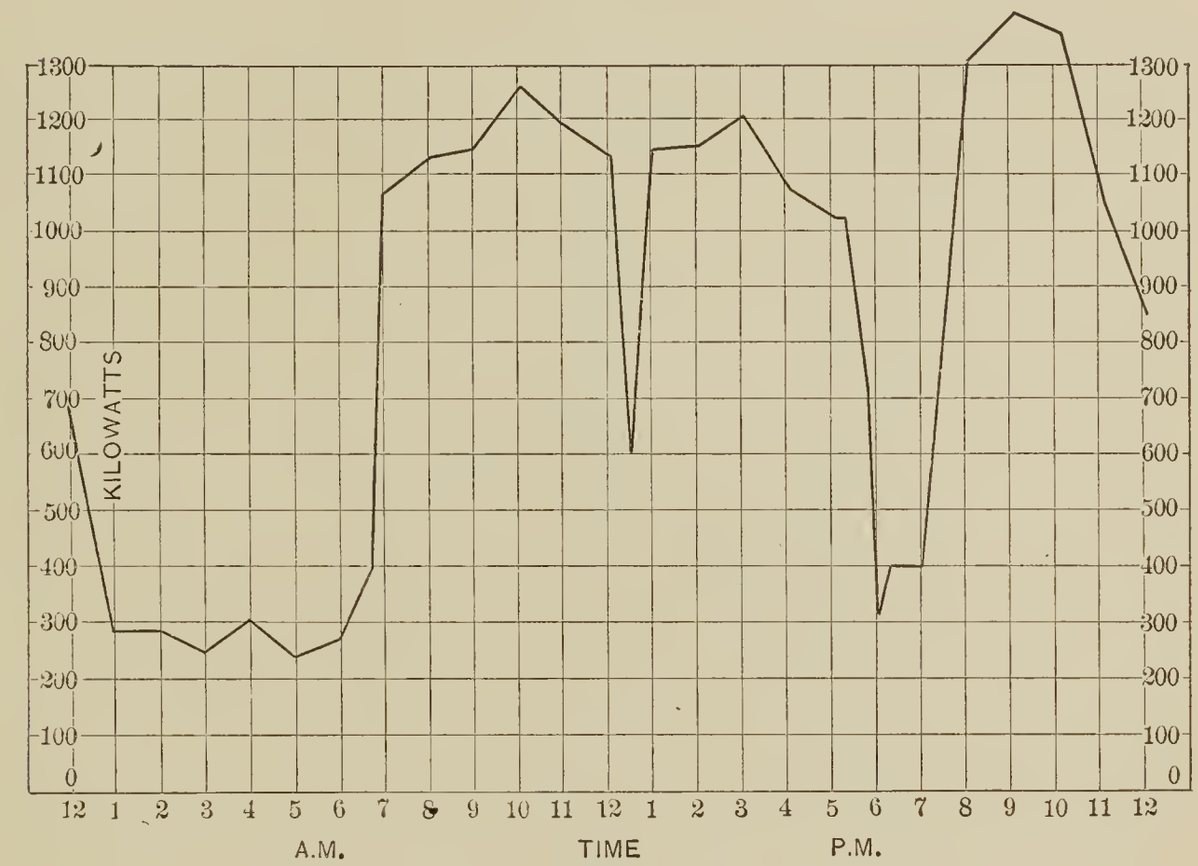


FIG. 2. Current generated June 13, 1906.

ranges of current utilization in order to meet the requirements of equalizing the load upon the station.

"As a matter of fact, electrothermic processes require for their successful and economical operation nearly continuous supply. The initial operation of bringing the furnace and materials up to the proper working temperatures may involve three times the energy required for their operation thereafter. Not only is this true, but the chilling and reheating of such furnaces is an operation quite as destructive to them as to the older types of apparatus.

"Electrolytic processes are mostly continuous. They depend

for their successful operation upon a certain ampère density at a fixed voltage, and from this it is obvious that the only method of control would be to cut out cells or sets of cells when the current supply must be reduced. Many of these operations are chemically reversible, and the effect of shutting down the process would involve considerable attendance.

"Barring out as impracticable the filling in of all the depressions in the load diagrams, it will be seen that either process could be supplied with a capacity of 240 k.w. for twenty hours

FIG. 3. Current available Dec. 15, 1905.

per day in winter and for twenty-four hours in summer, without exceeding the winter maximum peak of 1,643 k.w.

"It is also apparent that a capacity of about 550 k.w. could be supplied for seven hours per night at any period of the year.

"The addition of these processes to the system would place on the first chart an area of 8,650 k.w hours and on the summer chart an area of 9,610 k.w. hours.

"The suggestion has been made of the use of storage batteries for the purpose of handling electrolytic work. As the current for such purposes must be sold at a low rate and the storage

equipment is rather costly, this method of handling such a proposition would seem to merit little consideration.

While it may be possible to find processes to fit into the conditions shown in these diagrams, we have never seen anything of the nature of an efficient intermittent process.

"It may be concluded that electrothermic and electrolytic propositions must be considered on a straight twenty-four hour basis, and handled in all respects as any other business of similar load factors.

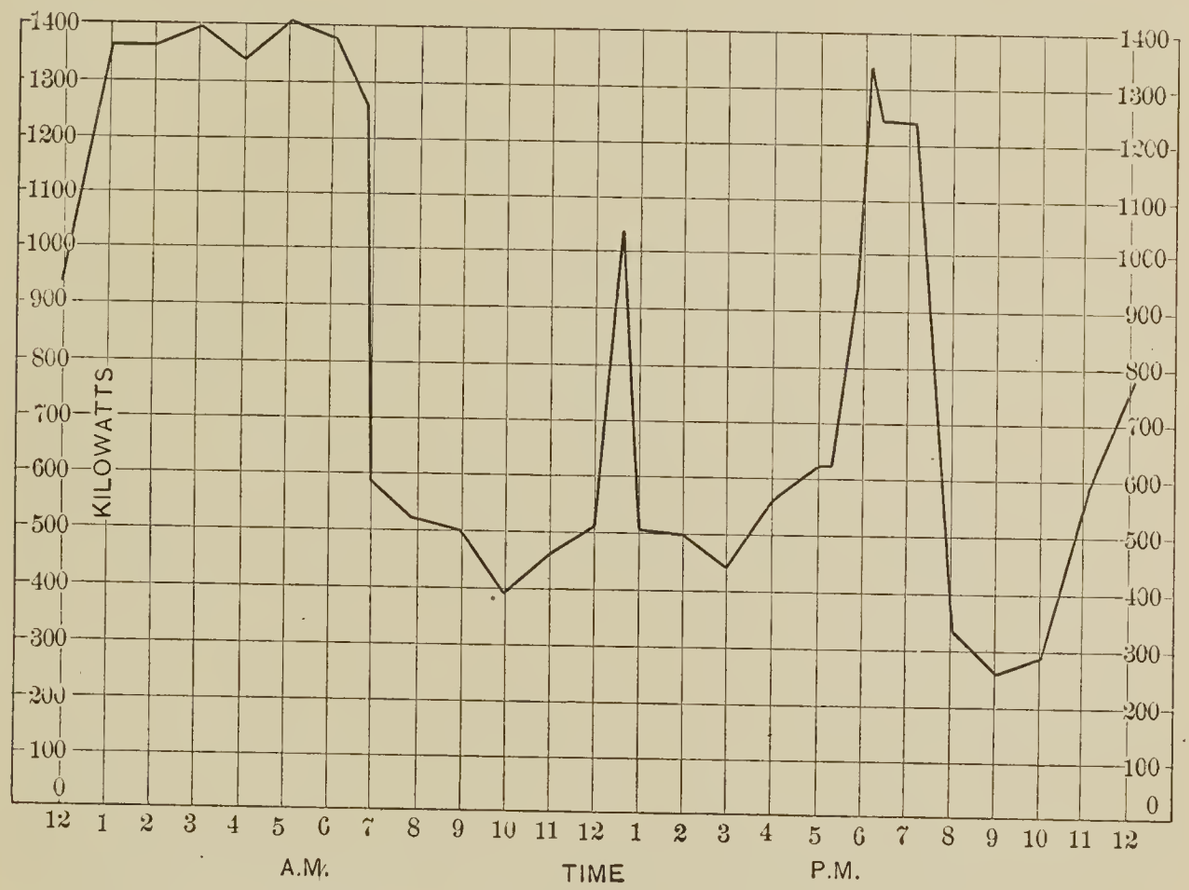


FIG. 4. Current available June 13, 1906; at maximum rate of Dec. 15, 1905.

"One of the most important points in connection with such processes as involve the supply of large volumes of electrical energy is the question of location with regard to the station. The elimination of distribution expense to a large extent, as well as the fact that the service investment would be very low, should make quite a difference in the rates central stations would offer to such industries as located in their immediate vicinity.

"While the tendency seems to be to locate such industries where water power is available, there are other factors which may help the central station to secure consideration in the matter

of current supply. The question of facility and low cost of transportation of raw materials and the location of principal market centers for finished product are important to any industry.

"While water power may seem reasonable, these items of expense may make central station service in some other and more favored locality the cheaper in the end.

"There are some electrochemical industries located now in out-of-the-way places which could obtain better results near some of our great shipping centers, for the reason that the cost of transportation of raw and finished product, plus the loss of certain by-products which cannot now be utilized, more than offset the advantages gained by the price of electricity at the present location. This condition of affairs was entirely unforeseen and those interested had no one to show them the great white way leading to the central station."

What has been done to develop electrochemical and electrometallurgical processes which can be made to fit into the valley?

What suggestions have been offered to central station men by which they may be able to load up their machinery during the off-peak hours? If, as has been suggested, the day is coming when the electrochemical men will have to depend upon the central station for their supply, what are we doing to further this matter?

Lower costs of generating current are the direct result of increased kilowatt hours, and are further enhanced by increasing the kilowatt hours on a fixed generating capacity. The central station has recognized this fact and are making rates based upon a fixed charge on the station and line investment for each kilowatt capacity and a rate per kilowatt hour for the current delivered.

The combination of these two produce the cost per kilowatt per annum.

If the electrochemical or metallurgical operation is of such a character that the station capacity used for light and power purposes during what we may term the peak hours is utilized for electrochemical and metallurgical purposes after the peak hours, then the charge for the kilowatt capacity may be eliminated. If, however, the operation must be twenty-four hours, the central station must recognize the investment charge made necessary by the capacity provided.

In all the papers that I have read on this subject, entirely too much stress has been laid on the cost per kilowatt hour, while there are other factors which enter into the question of the cost of the finished product.

The suggestions offered in this paper and in previous papers would seem to bear further investigation.

The author wishes to express his thanks for the suggestions offered to him from time to time by Mr. C. J. Russell.

DISCUSSION.

Mr. George Breed: There is one feature of this subject which all who are interested in electrochemical processes and inventions should keep before them, and this is the desirability of being able to suspend or retard a process for three or four hours a day without injury to the product or to the apparatus.

After considerable inquiry, I have found that the majority of those who use electrochemical processes insist upon having their full requirement of current uniformly supplied during the twenty-four hours of every day of the year. Under these circumstances, it is impossible for any ordinary electric light and power station to supply current at sufficiently low rates. In other words, we cannot take advantage of the low rates that many electric light and power companies would offer if it were possible to shut off or greatly diminish the current during the hours when a heavy electric lighting load must be carried by the power station; and consequently the process must be taken to some locality where electric power is unusually abundant; while coal is being burned in banked fires and millions of dollars worth of engines and dynamos are standing idle at an otherwise favorable location.

If processes could be modified so that this idle capital could be used, it would surely often be an advantage to the electrochemical manufacturer as well as to the electric lighting company. The ability to slacken or shut down a process even for say four hours after sunset on week-days during the four winter months, would frequently answer the purpose.

The inventor of a process is glad enough if it will work at all, but he should not be satisfied until it is fully in harmony with all commercial conditions; and the existence of cheap power available for processes that can be suspended for a few hours during the year is a most important condition.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 1, 1908; President C. F. Burgess in the Chair.

FORESTRY, WATER STORAGE, POWER AND NAVIGATION.

By Edward R. Taylor.

I make no apology for offering this paper to the American Electrochemical Society, for although we represent technical interests, we are not narrow men, but are interested in the development of our natural resources.

The man in the hill country hurries the water to the sea, while those in the Mississippi Valley build levees to keep out the floods that inundate their abundant and valuable lands.

It requires the broad man who is familiar with both conditions to solve the problem of floods and dry streams. "Look not every man on his own things, but also every man on the things of others" is appropriate here. No great good can be had without cost, and in a matter of this kind one part of the country must make a sacrifice (in a way) for a more valuable, though remote, interest.

The land, for example, in the Mississippi Valley is vast in extent and infinitely rich in quality if it can be protected from inundation. Levees have been raised until practically they have reached their limit.

Mr. O. M. Leighton, chief hygrographer, and A. H. Horton, in Forest Service Circular 143, have shown that it is perfectly practicable, in connection with the forestry service, to make larger or smaller lakes in the up-country and impound the water, so it will be held back in time of flood, and thus save the immense loss and damage that annually occurs on the Ohio and Mississippi rivers, and, at the same time, produce invaluable water powers and navigable rivers all through the dry summers. What is true of these rivers, is true of every river in the country to a greater or less extent. This is further elucidated in Forest

Service Circular 144, both of which circulars you are urged to secure from the United States Department of Forestry.

Having said this much as an introduction, I wish, in a brief way, to call your attention to the immense water-power possibilities of the State of New York. In the first place, if they were developed as they ought to be, they would be worth more than all the coal mines of Pennsylvania, and be of continual value for centuries after those coal mines, which are unrenewable, are exhausted. We have reason to be thankful that a few of our people are awaking to the importance of this great subject, but unfortunately, too many who are waking up are waking up only on one side of the question, and they think that one course of proceeding will handle the problem. This is notably true of *some* of those who are getting interested in forestry. Many think that forestry alone will do the whole thing; that is a great mistake.

We are here within 50 or 100 miles of the Adirondacks, and some New York advocates of forestry say: Reforest those mountains and you will do away with floods in the lower part of the river courses.

Reforestry will greatly mitigate the floods, but is only part of the treatment necessary.

My boyhood was spent on the lower course of one of the rivers having its source in these mountains, and more than fifty years ago, when the Adirondacks were practically all woods, I saw floods in that river that were appalling in their waste.

Two pictures of that stream at flood show a torrent of water pouring over the dam. While these pictures were taken in recent years, I have often seen as much water going over that dam in those days. I have hundreds of times, in the summer in my boyhood, walked almost all over the rocks as shown in the picture covered by that surging flood, and water so low that no power could be had for weeks at a time, which had more than anything else to do with my father leaving that place, in 1857.

We would not belittle the importance of forestry, but it is only part, though a very important part. The other part is the impounding of these flood waters in the up-country and where land is not so valuable.

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Now, this important and great end cannot be attained without cost, and right here is one place where we have the opposition of *some* foresters, namely, that lakes must be made in many cases, and perhaps in all cases, where some forests already exist, and the forester is unwilling that any part of the forest now standing should be sacrificed. It takes nerve to apply the knife when it is needed in surgery, and it takes nerve to apply the axe when it is needed in forestry. Has the forester the nerve to do it? No, not so long as he hugs the delusion that reforesting alone will stop the floods. While we are thankful that many of our people are being educated in forestry, they need to be able to see the other things, as well as forestry, and weigh them as they ought to be weighed.

As electrochemists, we are broad enough to be interested in this, though it is not either an electrical or a chemical subject, but it has much to do with our *power* to do things in the future, if not now.

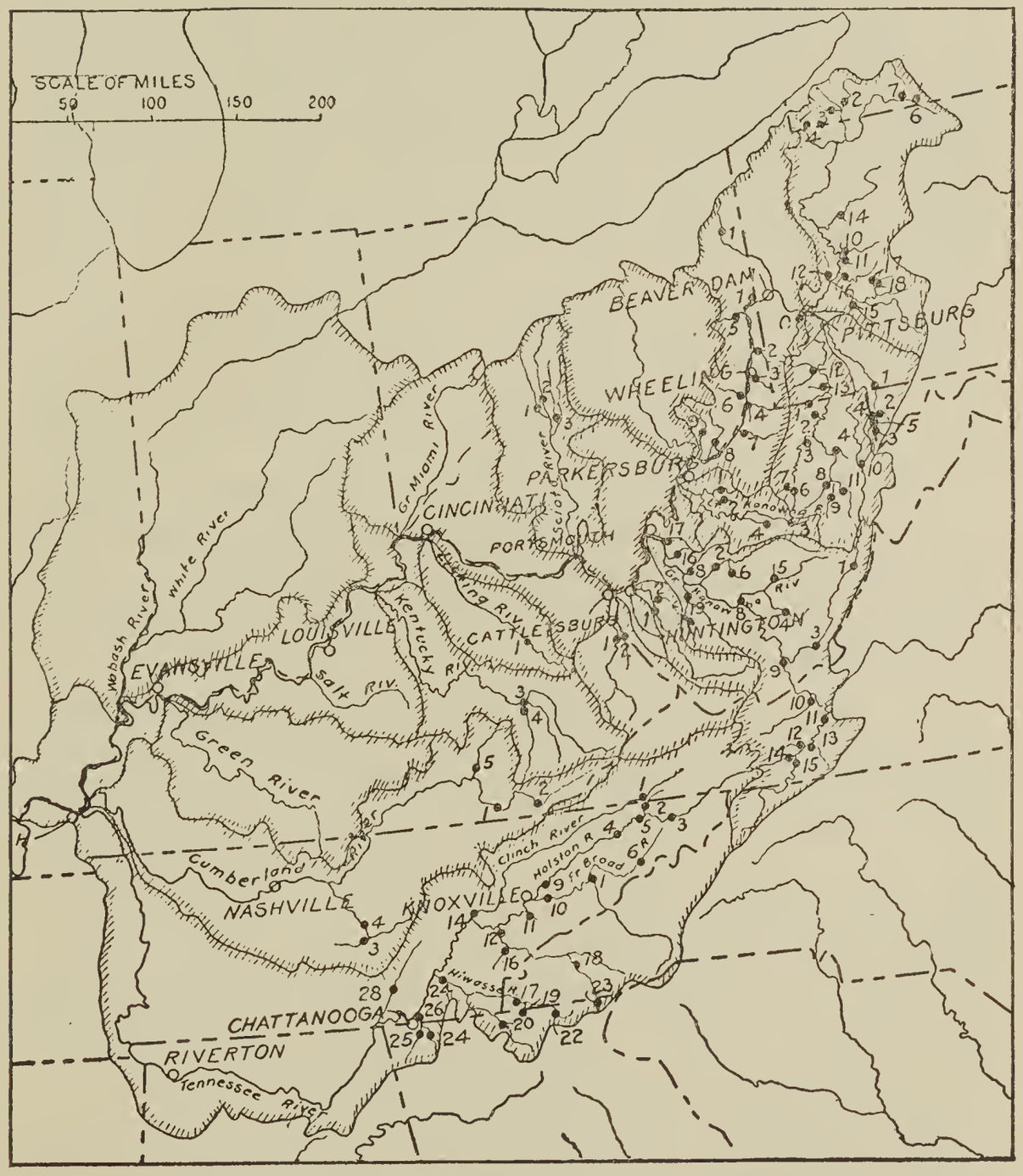
From the "World's Work," for March, is shown a map of the Appalachian watershed, showing the location of proposed lakes for impounding flood waters, and which, in connection with forestry, will make the Ohio River navigable for good-sized vessels the entire year and prevent the floods so destructive in that valley, while, at the same time, several million horse-power of water in the upper courses of the supply streams will be made available.

This also is illustrative of the conditions in the Adirondacks, and the cure would be the same. The cure would be expensive, but gone rightly about, the funds can be easily secured. One way is to stop immediately the disastrous floods by impounding the water in lakes in the head waters, and cut off the millions of dollars in loss by floods which our people suffer because of them. Let the State or the Nation advance the money to do it, and the people that are saved the floods will gladly pay the taxes to refund the State or Nation. The lumber that is cut to give place for lakes will give the forestry department money with which to reforest the districts now deforested, and the banks of the lakes will in a few years make cottage sites for all our people who want them.

But there is another means of paying for them. The user of power, and others who will come in to use it after it is made

available, will be only too glad to pay the expense of impounding the waters.

The Irrigation Department of our Government in the West has already solved what amounts to the same financial problem in advancing the money for the construction of reservoirs, to



be paid back by those benefited. Our problem is no more difficult and is as thoroughly practicable.

Fortunately, we have, in this State the New York State Water Supply Commission, who have this important matter in charge, and it is one of the objects of this paper to call your attention

to their work and to get ourselves in sympathy and in touch with the same and that of the general Government at Washington, whose frequent and valuable reports we should secure and study.

I quote only a few words from their second annual report, page 17: "The direct damage caused by floods in this State in a single year, according to the statistics reported by the State Water Storage Commission, has aggregated more than $3,000,000, besides the loss of life, physical and mental suffering, impairment of health, due to resulting unsanitary conditions, and the damage arising from interruption of public and private business, none of which could be assessed, computed or compensated.

Consideration of the problem of so regulating the flow of rivers as to reduce this menace makes clear the fact that in the minds of many it can best be done by storing up the flood waters, thereby making it possible to prevent the annual or occasional overflow, which brings about the conditions dangerous to health and property. It is admitted that such overflows have been endured for years without appearing a matter of serious import to the State, but that fact does not indicate that it deserves no consideration.

The storage of flood waters can only be accomplished by building storage dams at favorable reservoir sites and at a large outlay of money. The reservoirs once built, however, if properly located, might so control the flood waters of the rivers of this State as not only to minimize the danger to public health and safety, but to make them a constant source of advantage to riparian owners and to the State.

The law now provides that under certain conditions storage reservoirs may be built, and the cost thereof assessed upon the city, town, village and individuals benefited. * * *

"This will enable the State to sell the waters so stored to persons desiring their use, and make them a permanent and most important source of additional revenue. It seems to the commission that if the law were so amended that the State could control the flow of rivers and streams requiring such control, and could regulate the price at which such waters could be sold for power purposes, a valuable and permanent source of income would be secured.

Rivers are natural sources of material wealth, since their waters furnish power that can be easily and accurately measured and because they are constantly replenished by natural laws. Their flow is not uniform, however, and on this account many streams are unsatisfactory for power purposes, and are growing more so as the forests are cleared and fields improved. While nature has been generous, therefore, in providing our State with many and important rivers, she has also imposed a duty upon us if we would avail ourselves of these natural advantages. The problem to be solved is how to make the flow of these streams even and reliable. A proper solution will not only protect the public health and safety, but will make these streams productive of power of enormous value to the State. * * *

"It has been estimated by the State Water Storage Commission that water-power in this State could be made to produce an annual profit of $18,000,000, which equals, if it does not exceed, the net profits of agriculture in this State.

"The importance, therefore, of giving the subject early and careful consideration must be apparent."

This paper makes no pretense of treating this large subject. Its purpose is simply to call our attention to some sources of information that will help us all to form correct opinions and act upon these very important problems.

Take a membership in the American Forestry Association as a recreation, at $2.00 per year, and receive its twelve magazines, packed full of valuable information and pointing the way to more of the same sort.

Forestry, water storage, power and navigation, all working independently, would be grossly wrong, but all working together, as one, would be infinitely right, and nothing short of that would be right.

In no other place can money be more wisely expended or bring to the country such a magnificent profit.

The Forestry Department has called my attention to the valuable paper of Mr. Quick, in Putnam's, for April, being the fourth of a series of articles by him. It treats the subject admirably, and should be read by every one interested. The various circulars of the Forestry Department can usually be obtained gratis, by sending a request to Washington.

The Third Annual Report of the State Water Supply, just issued, speaks with no uncertain sound on the subject of impounding water.

On page 289, it says: "Coal once used is gone—but water, however often utilized, returns again—coal is growing less plentiful and more expensive—while water, by the processes of nature, keeps up its original force without additional cost." * * * *

"This is a plain statement of an almost elementary truth with which all who stop to consider our industrial conditions are familiar. This economic condition is attracting attention to the possibilities of the greater use of falling water and constitutes a summons to those in authority to provide a way to save the lost energy that is annually allowed to run to waste in our rivers.

"For years nature has presented the spectacle of wasted energy in water courses, and the action of the Governor and Legislature in directing so important a work as the conservation of this wasted power meets the hearty approval of all who have given the subject serious thought."

And on page 290, "The Sacandaga River rises in the Adirondack Mountains, its western branch in the south central part of Hamilton County, its eastern in the western part of Warren County, and it drains Lakes Pleasant, Piseco, Spy, Oxbow, Fawn, Elm, Sacandaga and others. The upper part of its water-shed is largely covered with forests, a great part of which are already owned by the State. These forests and lakes constitute of themselves natural reservoirs, and are so situated that with minimum effort their flood waters can be still more largely stored and made of practical use." * * *

"Above the proposed dam, the valley to be flooded consists of farms and swamps. Thousands of acres are covered with a thick, brushy growth of alders of little value. A large part of the soil still farmed is not valuable for such purposes. Evidence of the poor quality of it is seen at a glance, and no amount of industry can turn these sterile flats into productive areas.

"There are places where good farming lands are found, but in comparison with the great acreage of the valley these are few. Years ago, when timber was abundant and tanneries flourished, prosperous villages grew and thrived. But of late the opportunities for manufacturing and farming are so few that, except in

rare instances, a general depopulation has taken place, and this must continue. The mountains and hills forming the walls of the valley are either rock or glacial sand drift ; they are barren, steep, and contribute in no way to the thrift or prosperity of the occupants of the low lands. The river is subject to frequent spring and summer freshets, which often flood large areas and destroy such crops as the land might otherwise have produced. It is a delightful country to ride through, but a sterile one in which to make a living.

"From the work already done, it appears entirely probable that a safe and suitable site for a dam can be located at or near Conklingville, Saratoga County, that will cover an area of 40 square miles and store about 26,000,000,000 cubic feet of flood water; that the Sacandaga River thus dammed will furnish at this point a sufficient amount of water to produce 50,000 horse-power of energy, which is greater than the aggregate water-power of Lowell, Lawrence and Holyoke combined, or will increase the present available force at sites lower down the Hudson by 70,000 horse-power for the six dry months of the year." And on page 301,

"To acquire the dam sites and flowage rights on the large streams and begin the systematic building of storage dams at such places as will most quickly earn a revenue that will repay to the State the cost of acquiring such rights and of the necessary construction seems to the commission to be the plain duty of the State.

"There are obstacles to such an enterprise, but they are not insurmountable.

"In the area proposed to be flooded above the Sacandaga dam at Conklingville, there are about 100 acres of forest preserve land. The execution of this project will therefore require an amendment to the State Constitution respecting the flooding of State lands. The same is true of other available locations for storage dam sites in the Adirondack Mountains. In each instance the area of State land that would be flooded is small.

"An amendment to the Constitution that will permit the State to clear and flood State lands only where it shall be necessary to build storage dams in the interests of the people of the State and for a State revenue, these dams and reservoirs to be owned and

controlled by the State, would be required to meet the exigencies of the situation. It is for the people of the State to decide, in view of all the facts, as to the expediency of such action."

This last paragraph illustrates that 100 acres of timber land can completely block this great enterprise for the development in perpetuity of 50,000 horse-power of energy, and where the opposition of those who believe in Forestry only will be met.

A change of the State Constitution to meet these necessities is not easily obtained, with such opposition. Here we desire unity and the nerve to apply the axe for the greater good. Such a development on one of the smaller rivers will be an object lesson that will demonstrate the great value of the general application of water storage to all our streams, large and small. Indeed, there is sound sense in every farmer, where possible, developing the water-power that runs to waste through his own farm. It would be a help to all conditions of flood and power below.

Let each State or section develop one or two streams completely with forest and lakes (and even farmers' tributary brooks to be paid back at cost) as illustrations, and put them to work earning money to develop others later. Let co-operation be the watchword. Private interests cannot do it as it ought to be done; public interests must do it, and the doing will be immensely profitable and a benefit for all coming time.

P. S.—On going to Mechanicsville, N. Y., to visit the paper mill, on May 2d, the members of the American Electrochemical Society had a most practical and convincing object lesson in the principles set forth in the above paper. On this day six thousand horse-power was going through the water wheels, and sixty thousand horse-power was estimated as pouring un-used over the dam. At this same plant, in the summer time, the available water power is sometimes as low as two thousand, necessitating recourse to supplementary steam power. The flood water such as seen, flowing for one week, would supply the full requirement of the mill for ten weeks, if properly impounded and distributed. Surely, a moderate saving of this water at the head-waters would obviate

all shortage in the summer months. No more striking commentary on the reasonableness and practical utility of the principles advocated in my paper could possibly have been given to our Society.

P. S.—Since this paper was written the Forestry Department has called my attention to the valuable paper of Mr. Quick in Putnam's for April, being the fourth of a series of articles by him. It treats the subject admirably and should be read by every one interested. The Forestry Department have also kindly said they would send me Circulars 143-4, referred to the leaflet, "Wasting a Heritage," and some copies of Forestry and Irrigation, to which you are invited to help yourselves.

A lecture given at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 1, 1908; President C. F. Burgess in the Chair.

KINETIC MOLECULAR ENERGY.

By Charles P. Steinmetz.

A. HEAT ENERGY AND IRREGULAR MOLECULAR MOTION.

I. The fundamental laws of thermodynamics of gases are so closely related to physical chemistry and to electrochemistry that their consideration is of considerable interest to the electrochemist.

Many of the fundamental laws and premises of thermodynamics, however, are usually expressed in such form that it is very difficult, if not impossible, to get such a clear conception of them as required to thoroughly understand them, and the ability of handling them in mathematical equations does not mean physical understanding.

Such, for instance, is the case with the law, that, without expenditure of other forms of energy, heat flows only from higher to lower temperature, or with the assumption that in heating a gas, the heat energy divides in constant proportion between molecular and intramolecular or atomic motion. Especially the term *entropy,* while of great utility in theoretical thermodynamics, is a mathematical expression, of which an intelligent physical conception cannot well be formed.

II. To fully understand the changes brought about by heat, and therefrom the mechanism of transformation of heat energy into other forms of energy, and inversely, it seems to me necessary to consider the constitution of matter.

From philosophical conceptions, already in ancient times the theory was proposed that matter is not continuous, but consists of distinct small particles, separated from each other by spaces which are large compared with the size of the particles, the so-called molecules. This molecular hypothesis of the constitution

of matter has, in modern times, been reintroduced by the development of chemistry and physics, and almost become a certainty.

Assuming, therefore, the molecular theory of matter as the most probable and only satisfactory working hypothesis, it would, theoretically, not be possible to subdivide a piece of a substance indefinitely, but ultimately, further physical subdivision stops at the single molecule, which is the smallest particle of a substance. Chemically, the subdivision can still be carried further, to the atoms, which, by their chemical combination, in definite simple numbers, form the molecule. But the atoms which combine to the molecule of a substance are not the same substance, but are the chemical elements, which, by their combination, form the substance or the compound, and usually are of very different character therefrom. The molecule so consists of a number of atoms which are either all of the same kind or are different from each other. In the former case, the substance is called a chemical element, and the molecule usually consists of two atoms, rarely of more (as four in phosphorus, six in sulphur, three in ozone), or a single atom (as mercury, argon, helium, etc.). In the case of a molecule consisting of different atoms, the substance is called a compound, and the number of atoms in the molecule may vary from two up to many hundreds (in complex organic compounds), but is usually small, also.

Matter therefore is conceived to consist of smallest particles, or molecules, which, in their turns, are groups of atoms.

III. The forces of nature are universal in their application, and do not depend upon the sizes or dimensions of the bodies on which they act. The law of gravitation, across spaces of millions of millions of miles, regulates the relative motions of fixed stars, or across 100,000,000 miles of intervening space revolves the earth around the sun. The same law of gravitation must control the relative motions of the molecules of a body, though the molecules are so small and so numerous that the smallest part of matter, which can hardly be weighed by the most delicate balance, still contains millions of millions of molecules.

IV. As everything in nature, so the molecules of a body are in motion. This motion may either be regular motion or irregular motion. Regular motions are parallel motion of all molecules, at equal velocity in the same direction, rotary motion

of all molecules around parallel axes at constant velocity, etc. Motion of a mass is energy, and the motion of the molecules of a body so represents energy, the different forms of molecular motion, different forms of energy. The transformation of energy from one form into another then appears as a transformation of one form of motion into another form.

The particular mode of motion which represents a particular form of energy, as magnetic energy, etc., is unknown, except in few instances. For instance, parallel motion of all molecules at constant velocity is mechanical energy or momentum.

The molecular motion may be regular, that is, all molecules performing the same motion, or irregular, that is, different molecules move differently—in different directions, at different velocity, etc.

Some conclusions on the transformation of one form of molecular motion into another form appear obvious:

1. In any transformation of a regular motion into another form of regular motion, some of the motions of molecules lose their regularity, become irregular motion, the more, the greater the change in the character of regular motion, that is, the greater the difference between the two forms of regular motion.

2. This loss of regularity of motion must be especially large at the boundary line of the phenomenon, that is, at the boundary of the body which is the seat of regular motion.

3. The conversion of regular motion into irregular motion is complete, since it is merely the destruction of regularity.

4. Any conversion of irregular motion into regular motion must be very incomplete, that is, inefficient.

V. When considering the properties of the different forms of energy, we see that the above properties of the energy of irregular molecular motion are the characteristics of *heat energy:*

1. In any transformation of energy, some of the energy is lost by conversion into heat, the more, the greater the difference of the forms of energy, which are converted into each other.

2. The loss of energy by conversion into heat is especially large at the boundary of the phenomenon, the different forms of friction.

3. Conversion of energy into heat is practically complete.

4. All conversions of heat energy into other forms of energy are very inefficient.

The hypothesis that *heat energy* is the energy of the *irregular molecular motion* appears, therefore, strongly justified.

This brings us to the starting point of mechanical thermodynamics—the recognition of heat energy as the energy of irregular molecular motion.

B. PROGRESSIVE AND ROTARY MOLECULAR MOTION.

VI. Molecular motion may be *rotary motion,* that is, rotation of the molecules around an axis passing through the center of gravity of the molecule, or *progressive motion,* or a combination of both motions.

Both motions may either be *oscillating* or *continuous.* That is, the rotation of the molecule may be oscillating, the molecule revolving first one way, stopping, and then swinging back, stopping again and reversing, just as the oscillation of a pivoted magnetic needle. Or, the molecules may revolve continuously in the same direction.

The progressive motion also may be an oscillation, around a mean position, or a continuous progression in space.

VII. A molecule of a body, of mass m and velocity v, is acted upon by the force f, the resultant force exerted by the surrounding molecules. It therefore moves in a curved path, accelerating if the force f is towards the same direction as the velocity v, and retarding when its motion brings it into a region where the force f is in opposition to the velocity v. If the velocity v is small, the motion of the molecule is stopped in a region of opposing force, reverses and returns, so executing an oscillating motion.

If, therefore, the mean molecular velocity is low, the molecules perform oscillations, and their average relative positions thus are constant in space, the body has a constant shape and volume, that is, is a solid.

If the velocity v of the molecule is sufficient to carry it across the region of opposing force, until it again enters a region of assisting force and again accelerates, the molecule never returns to its former position, but moves constantly onwards, in continuous progressive motion, which, however, varies in velocity with the varying accelerating and retarding forces met by the molecule during its path.

VIII. At a certain definite mean molecular velocity, the

molecular orbits so change from oscillation around a fixed center to continuous progressive motion. In the latter case, the molecules no more have definite fixed positions with regard to each other, that is, the body has no shape, but is a fluid.

There is then a critical mean molecular velocity, v_1, and a corresponding heat energy, $\frac{mv_1^2}{2}$, of the molecules, at which a body changes from a solid to a fluid, and $v < v_1$, then corresponds to the solid, $v > v_1$, to the fluid state of a body.

IX. In this reasoning, the character of the forces acting between the molecules does not enter as essential element, except that these forces must be *central forces,* that is, the direction of the force between two bodies is the direction of the line connecting the bodies. The variation of the force with the distance, however, may follow the inverse square law, as with gravitation, or any other law may represent the decrease of the force with increase of distance.

C. STATES OF MATTER.

X. In heat engines, the carrier of the heat energy is almost always used in the fluid state, and the solid state of the matter is here of little importance. The molecular motion, which is of importance in thermodynamics, thus is continuous progressive motion of the molecules.

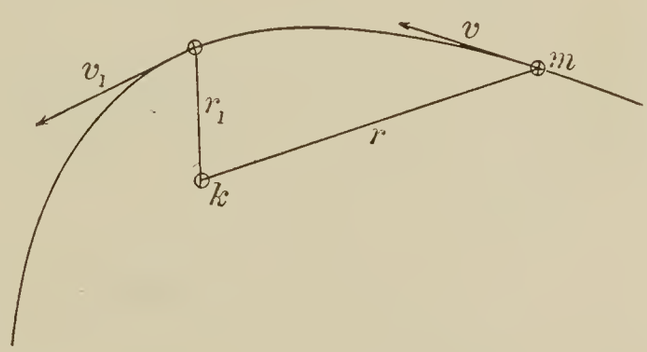


FIG. 1.

The laws of continuous progressive motion of bodies acting upon each other are the laws of astronomy determining the orbits of celestial bodies.

Considering first the simple case, of only two bodies acting upon each other,

XI Let, in Fig. 1, a body of mass m and velocity v be at-

tracted by a body of mass k, at distance r. (m may be the earth, and k the sun, or m and k may be two molecules of a gas or vapor.)

The kinetic energy, or momentum, of m is $\frac{mv^2}{2}$. The attractive force between m and k is proportional to the masses, and inverse proportional to the square of the distance (or any other function of the distance); hence, if a = gravitational constant,

$$f = \frac{m\,k\,a}{r^2} \tag{1}$$

Under the influence of this force f, the path of the mass m curves towards k (and inversely), that is, executes a curved orbit, as sketched in Fig. 1.

If now the body m approaches k during its motion, by dr, the work done by the attractive force f is:

$$f\,dr = \frac{a\,m\,k}{r^2}\,dr \tag{2}$$

During an approach of m to k, from the distance r to the distance r_1, the energy of the body m so has increased by

$$\int_r^{r_1} \frac{a\,m\,k}{r^2}\,dr \tag{3}$$

and therefore is

$$1/2\,m\,v_1^2 = 1/2\,m\,v^2 + \int_r^{r_1} \frac{a\,m\,k}{r^2}\,dr$$

$$= 1/2\,m\,v^2 + amk\left(\frac{1}{r_1} - \frac{1}{r}\right)$$

or,

$$v_1^2 = v^2 + 2\,a\,k\left(\frac{1}{r_1} - \frac{1}{r}\right) \tag{4}$$

If therefore

$$r_1 < r,$$
$$v_1 > v \tag{5}$$

that is, the velocity of body m increases when approaching, decreases when receding from, body k.

If

$$r_1 = r, \quad v_1 = v \tag{6}$$

that is, at the same distance from k, body m has again the same velocity. Or, in other words, when two bodies, as two molecules, approach each other, move around each other, and then recede again, they recede with the same velocity with which they approached each other. That is, the interaction of two bodies by the law of gravitation does not result in the transfer of energy from one body to another.

This is of importance in showing that whatever transfer of energy, and so equalization of speed, takes place between the molecules of a gas, must be due to the interaction by approach to each other of more than two molecules.

XII. It is of interest, however, to determine how far, when receding from each other, the two bodies m and k will separate, that is, whether m can move away into infinity or out of the range of attraction of k.

When receding to infinite distance from the attracting body k, $r_1 = \infty$, the velocity left to the body m is

$$v_1^2 = v^2 - 2\frac{ak}{r}$$

or,

$$v_1 = \sqrt{v^2 - \frac{2ak}{r}} \tag{7}$$

or, if both bodies have the same mass, m, as two molecules of the same gas, $k = m$, it is

$$v_1 = \sqrt{v^2 - \frac{2am}{r}} \tag{8}$$

If, therefore,

$v^2 < \frac{2am}{r}$, v_1 = imaginary, that is, the masses m can separate only a finite distance from each other, and then again approach.

If

$v^2 > \frac{2am}{r}$, $v_1 > o$, that is, the masses m move away from each other into infinite distance.

XIII. That means: If v = mean molecular velocity, r = mean molecular distance, and m = mass of the molecule, and a = gravitation constant, if

$$v^2 < \frac{2\,a\,m}{r}, \tag{9}$$

the molecules of the fluid cannot move away from each other beyond a finite distance, but circulate around each other in closed orbits, that is, have a constant mean distance from each other, and the body thus is a fluid of constant volume, that is, a liquid.

If

$$v^2 > \frac{2\,a\,m}{r} \tag{10}$$

the molecules of the fluid move away from each other into infinity, or until stopped by a boundary, that is, the body has no constant volume, but expands until it fills all available space. That is, the fluid is a gas.

The molecular velocity:

$$v_0^2 = \frac{2\,a\,m}{r}$$

thus is the velocity at which the fluid loses its volume, or the liquid turns into a gas, that is,

$$v_0^2 = \frac{2\,a\,m}{r} \tag{11}$$

is the characteristic of the boiling point of the substance.

XIV. According to the amount of heat energy contained by a body, or the energy of regular molecular motion $1/2\,m\,v^2$, three states of matter can be distinguished:

(1) v so low that the progressive motion is not continuous, but oscillating; constant shape and constant volume; solid.

(2) v sufficiently high to give continuous progressive motion, but $v^2 < \frac{2\,a\,m}{r}$; constant volume, but no constant shape; liquid.

(3) $v^2 > \frac{2\,a\,m}{r}$; neither shape nor volume constant, but body fills all available space; gas.

With increasing heat energy, that is, increasing temperature, the body so passes two critical points—the melting point, where

the oscillating progressive motion changes to continuous progressive motion, and the boiling point, where $v_0^2 = \frac{2\,a\,m}{r}$.

XV. NOTE: The conception of heat energy as irregular molecular motion is based on the consideration and comparison of the motions of numerous molecules, and so applies only to the consideration of the joint effect of numerous molecules. A single molecule in empty space may have a kinetic energy $\frac{m\,v^2}{2}$. but this energy is neither regular nor irregular, since there is nothing to compare it with. That is, a single molecule can have no heat energy, no temperature, and when coming to extremely high vacua, where the distances between the molecules are so large as to give an appreciable "free path," that is, where the action of individual molecules becomes appreciable, the conception of heat as a form of energy fails. So the cathode discharge in a vacuum tube cannot consistently be considered as having a "temperature."

XVI. From the equation of the boiling point,

$$v_0^2 = \frac{2\,a\,m}{r},$$

it follows that, decreasing r, the mean molecular distance, as by compressing a gas, increases v_0^2, and so the heat energy, or temperature $\frac{m\,v^2}{2}$ of the boiling point, and inversely.

That is—

The temperature of the boiling point increases with increase of pressure, and inversely.

D. ENERGY TRANSFER BETWEEN MOLECULES.

XVII. As seen, with two bodies acting upon each other by the law of gravitation, no energy transfer takes place, but the bodies recede from each other with the same kinetic energies, $\frac{m\,v^2}{2}$, which they had when approaching.

With three or more bodies acting upon each other, by the law of gravitation, or in general, under central forces, the dif-

ferential equations of their relative motion cannot be integrated in finite form. Some conclusions, however, can be derived directly from the differential equations. The most important, for the present investigation, is that energy transfer can take place between the bodies, that is, when three bodies approach each other simultaneously, and then recede from each other, the kinetic energy $\frac{m v^2}{2}$, of each of the three bodies is in general different when receding from the other two bodies, as it was when approaching them.

So, in the solar system comets coming from infinity have been retarded by the joint attraction of planet Jupiter and the sun, and thereby captured for the solar system, to revolve in elliptical orbits, until again their kinetic energy was changed by energy transfer from sun and planet, but this time increased, and the comet sent out again into infinity.

XVIII. Between the molecules of a body, transfer of energy so takes place whenever three or more molecules approach each other.

The result of this continuous transfer of energy between molecules must be that the molecules cannot all have the same kinetic energy, nor can the energy be distributed between the molecules in an irregular manner, but the distribution of kinetic energy between the molecules follows the law of probability. That is, if $E_1 = \frac{m v_1^2}{2}$, is the average, or algebraic mean of molecular energy, the velocity v_1 is the most frequent amongst molecular velocities. Velocities near v_1, either above or below, are nearly as frequent, but velocities far above or far below v_1 become less and less frequent, and velocities very much higher or lower than v_1 are very infrequent, but still exist, in accordance with the law of probability. That is, the distribution of velocity amongst the molecules is represented by a curve somewhat similar to Fig. 2.

XIX. The so-called mean or average molecular velocity, v_1, is not the arithmetic mean of all molecular velocities, but is the velocity corresponding to the arithmetic mean of all molecular

energies, $\frac{mv^2}{2}$, that is, V_1 is the *effective mean* or the square root of mean square of all molecular velocities.

The heat energy and the temperature of a body so is represented by the algebraic mean of molecular energies, $\frac{mv^2}{2}$, or

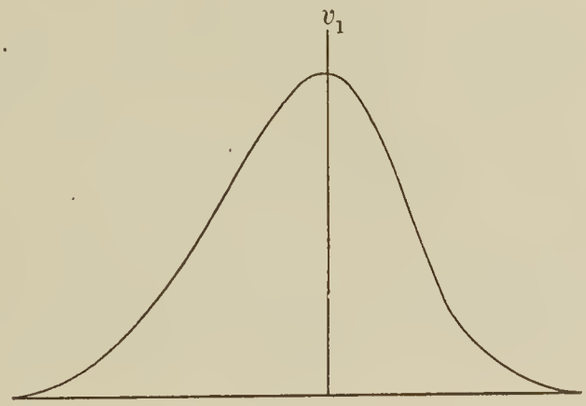


FIG. 2.

by the effective mean, that is, the square root of mean square of molecular velocities. When speaking, therefore, in the following of the mean molecular velocity, always the effective mean, or the square root of mean square, v_1 is to be understood.

XX. If, then, as shown in Fig. 3, the mean molecular velocity, v_1, is above the mean velocity, v_0, at the boiling point of the substance, that is, the substance is a gas, amongst the infinite

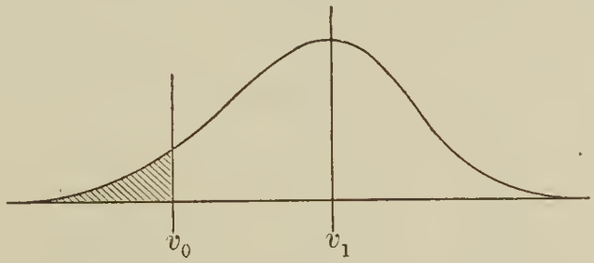


FIG. 3.

range of velocities of the molecules, velocities below v_0 also occur, the more frequent the nearer v_1 is to v_0. Molecules of velocities below v_0, when approaching the boundary of the vessel inclosing the gas, would not be able to escape, but remain. That is, gases condense on the surface of their containing vessels, the more the nearer the temperature of the gas is to its boiling point.

Two such molecules, of velocities below v_0, when coming near

to each other, that is, if by the interaction of three molecules two are left near each other, with relative velocities below v_0, are not able to separate from each other, but turn around each other in closed orbits, until, by the approach of a third molecule, they again receive energy to send them apart into space. Such groups of two molecules thus exist in a gas the more frequently the nearer the mean velocity v_1 is to that at the boiling point, v_0. As regards to space occupation, such a pair of molecules acts as a single molecule, that is, when approaching the boiling point, with decreasing temperature, a formation of an increasing number of such molecular groups occurs in the gas, that is, a partial condensation, resulting in an abnormal decrease of volume, and abnormal increase of density. As known, vapor density determinations very close to the boiling point are liable to be erroneous.

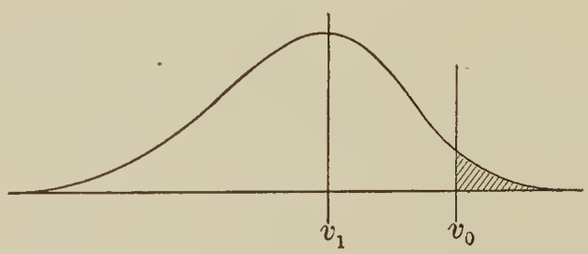


FIG. 4.

XXI. If in a body, v_1 is below v_0, Fig. 4, that is, the body a liquid or a solid, a certain greater or less percentage of molecules, as determined by the law of probability, have velocities greater than v_0. If such a molecule of a liquid or solid, which has an abnormally high velocity, greater than v_0, happens to be at the boundary of the body, and its velocity directed outward, it escapes from the body. That is, evaporation takes place from a surface of a liquid, and even a solid body, the more the nearer its temperature is to the boiling point. Incidentally, since only molecules of abnormally high velocity escape, their escape reduces the mean velocity of the remaining molecules. That is, the temperature of a body is reduced below that of surrounding space, by evaporation from its surface. Evaporation from the surface, below the boiling point, is the more rapid the nearer the mean molecular velocity of the body approaches that of its boiling point, but even liquids far below the boiling point, and

below the freezing point solids evaporate. So snow and ice gradually evaporate, and even metals, as zinc, show a slight evaporation at ordinary temperatures.

E. TEMPERATURE, PRESSURE, VOLUME.

XXII. If two gases of different molecular masses, m_1 and m_2, are mixed together, by the interchange of energy between their molecules, gradually their molecular energies equalize to the same mean value, that is,

$$\frac{m_1 v_1^2}{2} = \frac{m_2 v_2^2}{2} \qquad (12)$$

Where v_1 is the mean velocity of the molecules, m_1, v_2 the mean velocity of molecules m_2 (effective mean).

From this equation (12) follows

$$v_1 \div v_2 = \frac{1}{\sqrt{m_1}} \div \frac{1}{\sqrt{m_2}} \qquad (13)$$

That is, the molecular velocities of all gases which are mixed with each other are inverse proportional to the square root of their molecular masses, that is, molecular weights.

XXIII. All actions of gases which depend upon their molecular velocities, as diffusion through a porous diaphragm, therefore are inverse proportional to the square root of their molecular weight. So oxygen O_2, with a molecular weight 32, or 16 times the molecular weight of hydrogen H_2 (molecular weight 2), diffuses through a porous diaphragm $\sqrt{16} = 4$ times slower than hydrogen.

This law,

$$v_1 \div v_2 = \frac{1}{\sqrt{m_1}} \div \frac{1}{\sqrt{m_2}} \qquad (13)$$

permits the calculation of molecular velocities from molecular weights as soon as the molecular velocity of one body is given.

XXIV. By definition of the term "temperature," bodies have the same temperature if, when in contact with each other, no flow of heat energy occurs between them, that is, no interchange of heat. Gases which are mixed with each other thus have the same temperature. That is, all gases which have the same temperatures have the same $\frac{m v^2}{2}$ of their molecules.

The $\frac{m v^2}{2}$ of all gases thus is proportional to the temperature, and can be assumed as a measure of the temperature, and is used as such, as measure of the so-called absolute "temperature."

$$T = q \frac{m v^2}{2} \tag{14}$$

XXV. The impact, or moment, of a mass m at velocity v is m v. If n = number of molecules per unit volume of a gas, v the molecular velocity, the number of impacts of the molecules on unit area of boundary surface is n v.*

Since the impact force per molecule is n v, the total impact force, or pressure, exerted by the gas on unit area is

$$m v \cdot n v = n m v^2,$$

that is,

$p = n m v^2$ = pressure per unit surface of a gas of molecular mass m, molecular velocity v, and number of molecules per unit volume n.

Two gases, which have equal pressures,

$$p_1 = n_1 m_1 v_1^2 \text{ and } p_2 = n_2 m_2 v_2^2, \tag{15}$$

hence,

$$n_1 m_1 v_1^2 = n_2 m_2 v_2^2 \tag{16}$$

and equal temperature,

$$\frac{m_1 v_1^2}{2} = \frac{m_2 v_2^2}{2} \tag{17}$$

thus give, by dividing,

$$n_1 = n_2. \tag{18}$$

XXVI. From this, it results that any two gases, at equal pressure and equal temperature, have the same number of molecules per unit volume, n.

Since all gases, at equal temperature and pressure, have the same number of molecules per unit volume, the weight per unit volume of all gases, at equal temperature and pressure, that is, the specific weight of the gas is proportional to its molecular weight.

* While it is convenient, and for the present purpose permissible to speak of the "impact" of molecules on the boundary surface, the actual motion obviously is an orbital motion, and no more on impact than the motion of molecules around each other is an impact or a collision, as frequently stated for simplicity of expression.

The molecular weight of a gas thus is determined by measuring its specific weight.

XXVII. Since the pressure of a gas is

$$p = n\,m\,v^2,$$

and the absolute temperature,

$$T = q\frac{m\,v^2}{2}$$

it is

$$p = \frac{2}{q}\,n\,T \tag{19}$$

That is, the pressure of the gas is proportional to its absolute temperature at constant number of molecules n per unit volume, that is, at constant volume of the gas.

The volume of a constant mass of gas, that is, a constant number of molecules, obviously is inverse proportional to the number of molecules per unit volume, n.

$$V = \frac{S}{2n} \tag{20}$$

hence, substituting in (19),

$$p = \frac{R\,T}{V} \text{ or}$$

$$p\,V = R\,T \tag{21}$$

where R is a constant of the gas.

XXVIII. In two gases,

$$p_1\,V_1 = R_1\,T_1 \tag{22}$$

and

$$p_2\,V_2 = R_2\,T_2 \tag{23}$$

for the same pressure,

$$p_1 = p_2$$

and the same temperature,

$$T_1 = T_2,$$

it is, dividing (22) by (23),

$$\frac{V_1}{V_2} = \frac{R_1}{R_2} \tag{24}$$

XXIX. The specific weight of different gases at constant pressure and temperature that the weight per unit volume is

proportional to the molecular weight, since the number of molecules per unit volume is the same for all gases, and the volume per unit weight therefore inverse proportional to the molecular weights.

That is, if M_1 and M_2 are the respective molecular weights of two gases, V_1 and V_2, the volumes per unit weight at constant pressure and temperature,

$$\frac{V_1}{V_2} = \frac{M_2}{M_1} \tag{25}$$

hence, substituting in (24)

$$\frac{R_1}{R_2} = \frac{M_2}{M_1} \tag{26}$$

or,

$$R_1 = \frac{r}{M_1}$$

$$R_2 = \frac{r}{M_2}$$

and,

$$p\ V = \frac{r\,T}{M} \tag{27}$$

is the *fundamental equation of all theoretical gases,* where p = pressure per unit surface, V = volume per unit weight, T = absolute temperature, M = molecular weight, and r = a constant, which is the same for all gases, and is

$$r = 848,$$

if p is given in kg per m^2, V in m^3 per kg, T in centigrade.

XXX. That is, in all gases for a given quantity, that is, weight of gas, it is:

The pressure, at constant volume, is proportional to the temperature.

The volume, at constant pressure, is proportional to the temperature.

The pressure, at constant temperature, is inverse proportional to the volume.

The volume, at constant temperature, is inverse proportional to the pressure.

At constant temperature, the pressure at constant volume, or

the volume at constant pressure, are inversely proportional to the molecular weight.

Temperatures can therefore be measured by the change of pressure at constant volume, or by the change of volume at constant pressure.

XXXI. The absolute temperature, T, as measured by equation (27), becomes zero at —273° C., that is, the absolute temperature T counts from —273° C. as zero point.

At $T = O$, or —273° C., p and V would therefore be zero, and $\frac{m v^2}{2} = O$.

XXXII. In the preceding, the volume or space occupied by the mass m of the molecule has been neglected, as small compared with the space between the molecules, and the equations derived above therefore are approximate only, and have to be modified by correction for the actual space occupied by the molecules. Thus, for $T = O$ the volume V would not become zero, but only equal to the space occupied by the masses m of the molecules, if before this temperature were reached the character of motion has not already changed from that of a gas to a liquid and solid. For most practical cases, the correction for the mass of the molecules is so small that it can be neglected, except at very high pressure, and even then is not considerable.

The considerations of Section XX here also enter, as causing a deviation of the actual from the theoretical gas.

F. IRREGULAR ROTARY MOTION OF MOLECULES.

XXXIII. A mass k, attracting a mass m of relative velocity v and at distance r, causes it to swing around k in an orbit which depends upon v and r.

Suppose now the mass m consists of two separate masses m_1 and m_2 (or in general, a number of masses, m_1, m_2, m_3 . . .), then the two masses m_1 and m_2 traverse slightly different orbits, as shown by curves I and II in Fig. 5, and the mass, which approaches closer to k —m_1 in Fig. 5— reaches a higher velocity, that is, runs ahead of the other mass, m_2.

That means, if the masses m_1 and m_2 are not held together by forces acting between them, they separate when swinging around k.

In this manner, a swarm of meteorites, in its orbit around the sun, is gradually scattered along its path, and dissolves into a ring of meteorites, and comets are gradually disintegrated.

XXXIV. If the masses m_1 and m_2 cannot separate, but are held together by mutual attraction, the running ahead of m_1, when swinging around k, gives a rotary motion of m_1 around m_2. That is, a group of masses, $m_1 + m_2$, which is held together by mutual attraction—as the atoms of a molecule—receives a

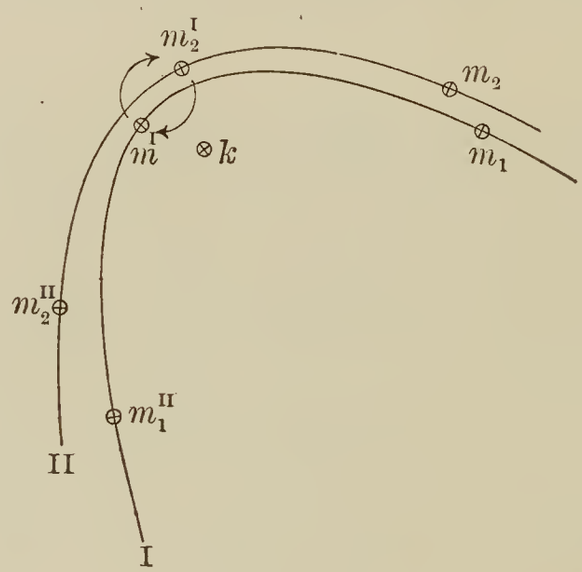


FIG. 5.

rotary motion when swinging around mass k, as another molecule. The energy of this rotary motion is derived from the energy of the progressive motion of masses m_1 and m_2; as separate masses, m_1 and m_2 would continue their orbits with the respective velocities v_1 and v_2, that is, the energies of progressive motion $1/2\, m_1 v_1^2$ and $1/2\, m_2 v_2^2$, held together by mutual attraction, the group $m_1 + m_2$ moves with the mean of velocities v_1 and v_2, that is, with velocity.

$$v = \frac{m_1 v_1 + m_2 v_2}{m_1 + m_2}$$

hence, with the energy of progressive motion,

$$\frac{m v^2}{2} = \frac{1}{2} \frac{(m_1 v_1 + m_2 v_2)^2}{m_1 + m_2}$$

and this resultant energy of progressive motion differs from the sum of the energies,

$$\frac{m_1 v_1^2}{2} + \frac{m_2 v_2^2}{2}$$

which m_1 and m_2 would have as separate masses. The difference is transformed into rotary motion.

If now the masses m_1 and m_2, when approaching k, already have a rotary motion around each other, this motion is either increased or decreased by the rotary impulse given by the motion around k.

That is,

When molecules consisting of several atoms,

$$m = m_1 + m_2 + \ldots$$

move around each other in their progressive motion, a transfer of energy takes place between irregular progressive motion and irregular rotary motion, that is, energy of progressive motion is converted into energy of rotary motion or "intramolecular" energy, so-called because it is energy of motion of the atoms in the molecule, or energy of rotary motion is converted into energy of progressive motion, until, by the law of probability, an equilibrium is established between the energy of progressive motion and the energy of rotary motion.

XXXVI. That is, the heat energy, or energy of irregular molecular motion, consists of the energy of progressive motion of the molecules, and the energy of rotary motion of the molecules, or intramolecular energy, and a constant proportion exists between the two quantities of energy of irregular motion, the rotary and the progressive. This ratio of energy of rotary motion and of progressive motion depends upon the number of atoms in the molecule, and is the larger the greater the number of atoms per molecule; it obviously equals zero if the molecule consists of a single atom.

XXXVII. When impressing irregular energy upon a gas, that is, heating the gas, a part of the energy thus appears as progressive motion, $\frac{m v^2}{2}$, so increasing the pressure p or the volume V, and another part appears as rotary motion, or motion of the atoms in the molecule, as intramolecular energy U. The latter is the greater, the greater the number of atoms per molecule.

XXXVIII. With increasing heat, and so increasing velocity of motion of the atoms in the molecule, a critical velocity so

must occur, at which the atomic velocity is sufficient to carry the atoms of the molecule away from each other, that is, the molecule flies asunder, or chemical dissociation takes place.

Chemical dissociation is thus, in the molecule, the analogous phenomenon to evaporation in the liquid.

G. INTERNAL AND EXTERNAL ENERGY OF A GAS.

XXXIX. A gas or vapor thus contains:

1. Energy of progressive irregular molecular motion,

$$M = \sum \frac{m v^2}{2} \tag{28}$$

2. Energy of rotary irregular molecular motion, or intra-molecular heat,

$$U = c M. \tag{29}$$

3. Position energy, that is, the energy representing the work done in separating the molecules of masses m by their distances r,

$$P = \int_{r_1}^{r_2} \frac{a m^2}{r_2} dr = a m^2 \left(\frac{1}{r_1} - \frac{1}{r_2}\right) \tag{30}$$

At the boiling point of a liquid, the molecular energy $\frac{m v_0^2}{2}$ is just sufficient to carry the molecules away from each other into infinity, that is,

$$\frac{m v_0^2}{2} = \int_{r_0}^{\infty} \frac{a m^2}{r_2}$$

$$= \frac{a m^2}{r_0} \tag{31}$$

That is, the energy of progressive motion of a liquid at the boiling point, M, equals the position energy of the gas produced from the liquid, at infinite volume, that is, infinite molecular distances.

In changing to a gas, at the boiling point, position energy P is therefore produced, and this energy is taken from the energy of irregular motion, M and U, in proportionate amounts, since $U = c M$.

If the gas shall have the same temperature as the liquid, energy therefore must be supplied to restore the M, and therefore the U, to the same value as before.

XL. When converting a liquid of temperature T_1 into a gas of temperature T_2, energy thus is required:

1. To change the temperature of the liquid from T_1 to the boiling point, T_0, that is, increasing the energies M and U of the liquid.

2. At the boiling point, T_0, if $r_0' =$ mean distance of the molecules of the liquid, $r_0 =$ the mean distance of the molecules of the gas at the same temperatures, the position energy,

$$P = \sum am^2 \left(\frac{1}{r_0'} = \frac{1}{r_0}\right)$$

is required to carry the molecules away from each other from distance r_0' to distance r_0 without changing their energies, M and U. Or rather, the molecules are carried away from each other from distances r_0' to distance r_0 by a conversion of energies M and U into position energy P, and the energy M and U, which so has been expended, is to be supplied to the gas.

3. When changing from a liquid of volume V_0', to a gas, of volume V_0, at the same pressure, p_0, the surrounding space has to be pushed away, that is, external work done, and so the energy is required,

$$W = p_0(V_0 - V_0').$$

4. To increase the temperature of the gas from the boiling point, T_0, to the temperature T_2, the energies are required:

M_0'', to increase the progressive molecular motion or molecular energy.

U_0'', to increase the rotary molecular motion or intramolecular energy.

P_0'', to increase the position energy, by increasing the molecular distance from r_0 to r_2.

W_0'', to do the external work in increasing the volume from V_0 to V_2.

XLI. Assuming that a gas changes from a pressure p_1 and volume V_1 to pressure p_2 and volume V_2. Let, at any moment, $p =$ pressure, $V =$ corresponding volume. An increase of volume V by d V, against pressure p, then requires the energy,

$$dW = p\,dV, \qquad (32)$$

and a change from p_1, V_1 to p_2, V_2 so requires the expenditure of the energy.

$$W_1'' = \int_{p_1}^{p_2} p \, d V \tag{33}$$

This is the external work done.

The heat energy of evaporation so consists of position energy P, external work W, or is

$$L = P + W. \tag{34}$$

This is called the *latent heat of evaporation,* since it is not felt, that is, does not result in a change of temperature, and P is the *internal,* W the *external,* L the *total* latent heat of evaporation.

Specific Heat of a Gas.

XLII. In a liquid, the energy required to raise the temperature of unit weight by 1° is called the specific heat, c, of the liquid. It is definite, that is, depends only on the character of the liquid and the temperature, T.

In a gas, the specfiic heat, that is, the energy required to raise the temperature of unit weight by 1°, is not definite, but depends upon the condition under which the temperature is raised. The gas equation is,

$$p V = R T,$$

and an increase of temperature T so results in a change of pressure p, or change of volume V, or both, and depends upon the relative change of p and V. So different specific heats exist for a gas.

XLIII. If, during the change of temperature, the volume remains constant, thus the pressure only changes, the external energy, W, and the position energy, P, are zero, and only the molecular energy, M, and the intramolecular energy, U, is required. That is,

The specific heat at constant volume, c_v, is the molecular and intramolecular energy, M + U, required to raise unit weight of a gas by 1° of temperature.

XLIV. If, during the change in the temperature, the pressure remains constant, but the volume increases, in addition to the molecular and intramolecular energy, M + U, the position

energy, P, is increased, by the increasing distance between the molecules and external work done;

$$W = p(V_2 - V_1),$$

that is,

The specific heat at constant pressure, c_p, is the molecular energy M, the intramolecular energy U, the position energy P, and the external energy W required to raise unit weight of a gas by 1° of temperature.

That is,

$$c_p = c_v + P + W$$

XLV. For a given gas, M and U are proportional to each other.

The position energy, $P = \sum am^2 \left(\frac{1}{r} - \frac{1}{r'}\right)$, is proportional to M, since for $r' = \infty$, $P = M_0$, the energy M at the boiling point.

The external energy, $W = p(V' - V)$, is proportional to the temperature, and so the M. That is, all four energies are proportional with each other, with factors of proportionality depending on the number of atoms in the molecule, and the two specific heats, c_p and c_v so are proportional to each other.

XLVI. In addition to c_p, at constant pressure, and c_v, at constant volume, an infinite number of specific heats, c_{pv}, exist, each defined by an equation existing between p and V during the change of temperature. That is,

If $f(pV) = o$ is any function of p and V, the specific heat c_{pv} is the energy required to raise unit weight of a gas by 1° in temperature, while p and V change relative to each other by this equation.

H. EXPANSION CURVES OF A GAS.

XLVII. A gas, as seen, has three variables, p, V and T, of which two are independent variables.

Any change of condition of a gas is therefore definite only if one independent equation is given between the three variables, p, V and T.

The most important of these conditions are:

XLVIII. A.

$$T = \text{constant},$$

that is,

$$p\,V = R\,T = \text{constant}; \qquad (35)$$

or,

p and V change inverse proportional to each other, that is, the p V curve is represented by an equilateral hyperbola.

This change at constant temperature, T, is called *isotherm.*

A change of gas at constant temperature leaves M, and therefore U, unchanged. With decreasing p and increasing V, the position energy, P, and the external work, $W = \int p\,d\,V$, are required.

That is, expansion of a gas at constant temperature, or isotherm expansion, requires energy input, the energy P + W. Inversely, isotherm compression of a gas requires abstraction of energy, or cooling.

XLIX. B.

Change of p and V without input or abstraction of heat energy.

If, during the expansion of a gas, that is, increase of volume V and decrease of pressure p, no energy is put into the gas, the energy P + W, required by the increase of volume, must be supplied by the internal energy M + U, that is, M + U decreases, or, in other words, the temperature T—which is proportional to M—falls. That is, expansion of a gas without addition or subtraction of heat energy results in a decrease, compression in an increase of temperature. Such a change at constant total energy, M + U + P + W, is called *adiabatic,* or *adiatherm.*

It is of foremost importance, since it is the change taking place in a gas when left to itself and doing external work in a heat engine, or receiving external work in a compressor.

L. The fall of temperature T results from the supply of energy P and W by the energy M + U. The smaller, therefore, the intramolecular energy U is, the greater must be the decrease of the molecular energy M, that is, the more the temperature T falls, with adiabatic expansion.

The decrease of temperature T results in a decrease of volume, or of pressure, below that corresponding to constant temperature or isotherm condition.

That is, the adiabatic curve deviates the more from the isotherm the simpler the molecule of the gas is, that is, the less atoms per molecule it has. Assuming a gas of an extremely large number of atoms per molecule, the intramolecular energy U would be very large compared with the molecular energy M, and U would so supply nearly all the energy P + W, that is, M, and so the temperature T, would decrease very little with the adiabatic expansion, or the adiabatic curve would approximate the isotherm,

$$p V = \text{constant}.$$

With a monatomic gas, where U = O, all the energy, P + W, must be supplied by M, that is, the temperature T falls most, during adiabatic expansion, and the volume so increases far less than it would on the isotherm curve.

LI. To investigate these relations further, let

$$c = \frac{U}{M} = \text{ratio } \frac{\text{intramolecular}}{\text{molecular}} \text{ energy}$$

where c = O for a monatomic gas, as argon, helium, mercury;

c > O for a gas having several atoms per molecule, and the greater the larger the number of atoms.

Assuming unit weight of gas, of pressure p, volume V, temperature T, and let

r = mean molecular distance, m = molecular mass, n = number of molecules per unit volume.

From the preceding equations, the change of the component energies, M, U, P, W, resulting from a change of volume d V, can then be derived, and as in adiabatic expansion, the total energy is constant, the sum of these changes of energy resultant from a change of volume d V, must equal zero. This gives finally the equation,

$$p V^{\frac{1 + c + 2/3}{1 + c}} = \text{constant} \qquad (36)$$

The Equation of Adiabatic Expansion.

1 + c represents the energy of irregular molecular motion M + U.

⅔ represents the energy of position and of external work P + W.

LII. The specific heat at constant volume, c_v, is proportional to M + U, hence to 1 + c.

The specific heat at constant pressure, c_p, is proportional to $M + U + P + W$, hence to $1 + c + 2/3$, and the exponent, therefore,

$$\frac{1 + c + 2/3}{1 + c} = \frac{c_p}{c_v} \tag{37}$$

or is the ratio of specific heat at constant pressure and at constant volume.

That is, the adiabatic curve is

$$p\,V^{\frac{c_p}{c_v}} = \text{constant} \tag{38}$$

LIII. Denoting,

$$\frac{c_p}{c_v} = \frac{1 + c + 2/3}{1 + c} = a \tag{39}$$

it is

$$p\,V^a = \text{constant.} \tag{40}$$

The equation of the adiabatic or adiatherm curve, that is, the curve of expansion or compression without adding or subtracting heat energy, that is, change in which the external work is done by or converted into molecular and intramolecular energy.

LIV. For a monatomic gas, $U = O$, and therefore $c = O$.

For a diatomic gas, as oxygen, nitrogen, air, carbon monoxide, etc., the energy of motion of an atom around the single other atom of the same molecule should be half the energy of motion of the atom around the two atoms of another molecule. That is, per atom, the intramolecular energy is one-half the molecular energy. That is, $U = \frac{1}{2}M$, or $c = .5$.

For a triatomic gas, as carbon dioxide, water vapor, etc., the intramolecular energy may be assumed as twice, for a 4-atomic gas, as ammonia, as 3 times that of a diatomic gas, that is, $c = 1$ for a triatomic, $c = 1.5$ for a 4-atomic gas, etc.

Hence,

monatomic gas	$c = O$	$a =$ 1.667,	argon, helium, mercury.
diatomic gas	.5	1.445,	air, nitrogen, hydrogen, CO.
triatomic gas	1.0	1.333,	CO_2, water vapor.
4-atomic gas	1.5	1.265,	ammonia.
9-atomic gas	4	1.133,	alcohol.

23 to 26 atomic gas, 11 to 12.5, 1.0555 to 1.0494, gasoline.

LV. These relations between the numerical values of U and M, and the values of c and a derived therefrom, do not strictly apply any more, however, if the atoms in the molecule are unequal in weight and if different forces act between the atoms of the molecule. So, for instance, in water vapor, H_2O, one of the atoms, O, has 16 times the mass of each of the other two atoms. This would have the effect, probably, of increasing the value of a, or decreasing U and c. The forces acting between the two H atoms and the O atom of the water molecule are, however, chemical forces also, and the attraction between H and O therefore greater than the gravitational forces. As result thereof, the intramolecular motion of the atoms would represent a greater amount of energy than corresponds to the number of atoms, and U and c would therefore be greater than corresponds to a triatomic gas, that is, a smaller, the more so the greater the chemical forces. Hence, elementary gases deviate less from the theoretical constants than compounds.

Unequal sizes of atoms therefore increase, chemical forces between the atoms—as in H_2O— decrease, the adiabatic constant a.

LVI. It is obvious that the preceding can be only a tentative outline of a *mechanical thermodynamics.* It is interesting, however, to see that it seems possible to derive the laws of thermodynamics from the law of central forces acting between molecules and atoms, without any other assumption as regard to shape, elasticity of molecules, etc., and also without introducing terms as entropy, in short, that it should be possible to entirely eliminate *heat* as a separate and specific form of energy, and treat *thermodynamics* merely as the *theory of irregular mechanical motion,* that is, as a part of *mechanics.* Hereby not only the deviation of the performance of gases from that of the theoretical gas, as resultant from finite size, polymerization, dissociation, unequal masses of the atoms in the molecule, chemical forces acting within the molecule, etc., may be explained, but it may be possible even to calculate the numerical values of these deviations.

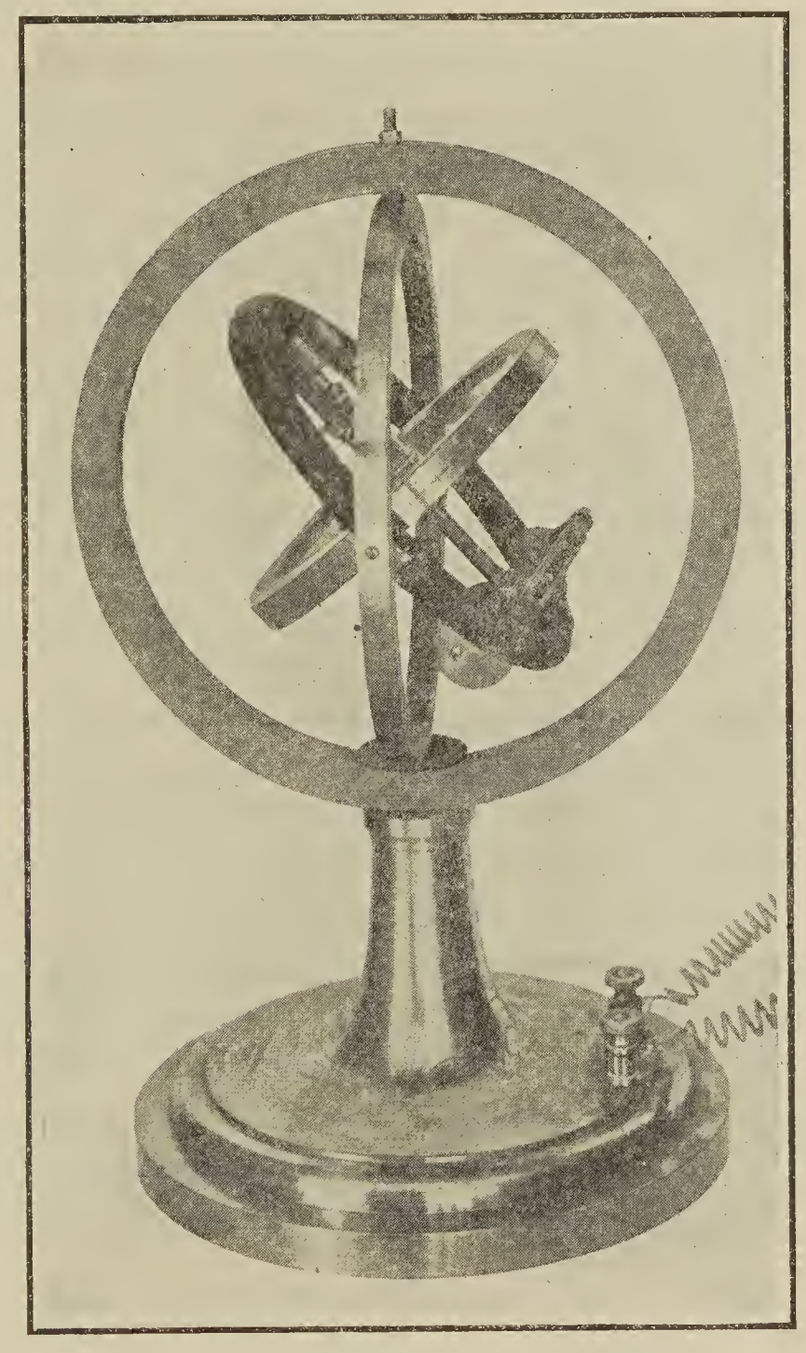
DISCUSSION.

Mr. Edward Durant *(communicated)*: Prof. C. P. Steinmetz's lecture is an endeavor to eliminate the conception of entropy, by substituting a formula that would be practically a constant in problems involving the basic law of chemistry, but when he applies the same mode of reasoning to planets, comets and moons or celestial electrons, he opens the door for a discussion upon a law governing the kinetic or physical universe. When we consider the initial heat, variation of temperature, also the compressibility, weight and density of mass, it is apparently from a relative or local point of view. But when we theorize from a universal standpoint, it seems to me that we may consider nothing in the universal formulæ except time, matter and motion. The new mechanical motion discovered in the electrically-operated gyroscope (see Scientific American, July 15, 1905) proves that any substance, body or mass spinning with sufficient speed to move in an orbital plane continues to move in the same plane forever. It also shows that the weight or gravitational influence is controlled from the center of the orbit, making it plain to the eye and to reason that weight, gravity, heat, variations in temperature, entropy and mass are irrelevant.

GYROSCOPE.

This gyroscope is, in fact, another satellite to this earth, and my suggestion would be that it be considered a negative electron or corpuscle model. I believe the law is, the cube of the square root of mean radius vector equals the unit of orbital time. This is in exact accord with the electron theory advanced by Prof. J. J. Thomson, and it simplifies it to the extent that we need not consider the volume, shape, weight or number of electrons in an atom. To still further substantiate this theory, I might state that in Newton's terrestrial gravitation law and in his so-called first celestial gravitation law (Prop. 4, Cor. 6, Book 1, Newton's Principia), he does not mention the words gravity, weight, entropy, mass or volume. He merely mentions bodies, meaning substances or matter in motion. Galileo and Kepler merely consider time and matter in motion. In conclusion, I

might make clearer my theory by giving one example. Suppose an electron or planet A has a mean unit radius vector of 4 units of length, then the orbital time is the square root of 4, which is 2, brought up to the third power, which equals 8. Under the



same ruling, a planet or electron B having a mean unit radius vector 16 will have 64 for its unit of orbital time. The square of the orbital time 8 of electron or planet A is the square of the orbital time 64 of the electron or planet B as the cube of the mean unit radius vector 4 of the electron or planet A is to the cube of the mean unit radius vector 16 of the electron or planet

B. Or, in other words, it is in exact accord with Kepler's Law of Astronomy.

Dr. Jos. W. Richards *(communicated)*: Dr. Steinmetz has shown in one way the relations between specific heat of gases at constant pressure and at constant volume, perhaps we might say from the electrician's point of view. As a chemist, I have accustomed myself to looking at them from a slightly different viewpoint, which may make the matter clearer to some here present, but which amounts to the same thing in the end.

If a molecule is considered, that is, that particle of a substance whose mode of motion constitutes the measure of its temperature, the amount of heat simply necessary to raise its temperature 1° C. is 3 calories, leaving out all other work, but the mere increase of temperature energy. This statement needs explanation, for the non-chemist, by saying that the 3 calories are needed to raise the temperature of molecular weight in grams, 1° C. This would be, for instance, the specific heat of 200 grams of mercury vapor, or 65 grams of zinc vapor (which are monatomic vapors), at constant volume.

Considering the same quantity of material, in the gaseous state, its volume at standard conditions is a constant, 22.22 litres, and the outside work done in increasing its temperature 1° C. is represented by the increase of 1/273 of 22.22 litres in volume, against atmospheric pressure, which represents 2 calories.

If the molecule is complex, and not monatomic, the increase of temperature does internal work in the molecule, which is found to be $2(n - 1)$ calories per degree, n being the number of atoms in the molecule.

We have, therefore, to raise the temperature of molecular weight of a gas 1° C., the following quantities of heat required:

N = No. of Atoms in the Molecule	Temperature Energy	Intra-Molecular Energy	Outer Work	Total
1	3	0	2	5
2	3	2	2	7
3	3	4	2	9
4	3	6	2	11
5	3	8	2	13

The ratio of specific heat at constant pressure to specific heat at constant volume follows directly from the above numbers. It is as follows:

N = No. of Atoms in the Molecule	Sp. Heat at Constant Pressure	Sp. Heat at Constant Volume	Ratio = K
1 (Mercury, Vapor, etc.)	5	3	1.67
2 (Hydrogen, Air, etc.)	7	5	1.40
3 (CO^2, SO^2, etc.)	9	7	1.29
4 (SO^3, NH^3, etc.)	11	9	1.22
5 (CH^4, SiH^4, etc.)	13	11	1.18

Dr. C. P. Steinmetz *(communicated):* Dr. J. W. Richards' remarks are extremely interesting in showing the general nature of the quantitative relations between the components of molecular and intramolecular energy, which can be understood only if these energy components are the results of a general law of nature, as the law of gravitation. The values of the constant a, given by Dr. Richards, differ somewhat from those given in LIV of my paper, and agree even closer with experimental results. They follow the same equation (37) of my paper, but with the value of the constant: $c = \frac{2}{3}(n-1)$, while I assumed $c = .5(n-1)$, where n = number of atoms in the molecule. By a slight modification of the reasoning, Dr. Richards' value of c can be derived from the argumentation of the paper, and thereby the agreement of the theoretical values of a with the experimental data be increased.

Mr. E. Durant's discussion of the similarity of the molecule with the gyroscope and the electron, appears to me, however, a metaphysical speculation, and, as such, a matter of belief rather than science.

Abstract of paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., April 30, 1908; President C. F. Burgess in the Chair.

THE ABSORPTION OF THE RADIO-ACTIVE EMANATIONS BY CHARCOAL.

By R. W. Boyle, M. Sc.

Charcoal, especially that of cocoanut, readily absorbs gases, and this property holds for the radio-active emanations

This work is an attempt to find the laws which the phenomenon obeys, and is done mostly with the emanation of thorium by a flow method of experiment.

The results of the work so far may be summed up as follows:

The amount of absorption depends on—

(1) The nature of the charcoal used, being greatest for cocoanut, intermediate for animal, and least for wood charcoal;

(2) The extent of the charcoal absorbing surface, the greater the surface the greater the absorption;

(3) The temperature of the charcoal, thus following the law for ordinary gases, viz.: a lowering of the temperature causes an increase and a raising of the temperature a decrease in the amount of absorption;

(4) The velocity of the current of gas which conducts the emanation through the charcoal, the absorption being greatest at the slowest possible speeds.

McGill University,
Montreal.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 1, 1908; President C. F. Burgess in the Chair.

ELECTROCHEMICAL PATENTS, AND SOME NEEDS OF THE UNITED STATES PATENT SYSTEM.

By Arba B. Marvin, Jr.

When our forefathers framed the Constitution of the United States, they introduced a simple little clause, which reads: "The Congress shall have power * * * * to promote the progress of Science and useful Arts, by securing, for limited Times to Authors and Inventors the exclusive Right to their respective Writings and Discoveries."

This clause is simplicity itself, and yet, based on it alone, there has grown up the wonderful patent system of the United States, a system more complete and more powerful than that of any other country. This clause has proved operative, in a most efficient way, in promoting "the progress of Science and useful Arts."

There was, in colonial times, little need for a complex patent system. The country was new and undeveloped, manufactures almost unknown, and men too busy struggling against the forces of nature to have either time or energy for developing the sciences and useful arts. Even the framers of the Constitution, wise and skillful statesmen though they were, could not have foreseen the great future of this innocent-looking clause, nor foretold the development a century would bring.

To Congress was left all details of form and procedure, and out of Congressional enactment has grown the host of rules and principles which now make up the law of patents.

At the first meeting of Congress, effort was made to put into operation the powers granted by the Constitution for the encouragement of inventors, but the bill was regarded as of little importance, and never came up for final consideration. At the

next session, in 1790, President Washington, in his first message to Congress, said:

"I cannot forbear intimating to you the expediency of giving effectual encouragement as well to the introduction of new and useful inventions from abroad as to the exertions of skill and genius at home."

Three days later the committee on unfinished business resurrected the bill of the previous session. After discussion and amendment, that bill became a law.

This law of 1790 was simple, but so were the needs of the country. No provision was made for a patent office, nor for patent examiners, and none was necessary. If a man desired a patent, it was only necessary for him to fully disclose his idea, whereupon a cabinet meeting was called, and the Secretary of State, Secretary of War and the Attorney-General considered the advisability of granting to the applicant the exclusive right contemplated by the Constitution.

The issue of a patent was a solemn affair. It meant the granting of a monopoly. For the period of fourteen years, the inventor alone could practice the new art, or make, use or sell the new machine or manufacture. The statesmen of that period were too strongly imbued with the traditions of England to consider lightly the granting of a monopoly even for so simple a thing as an improved scythe or a new method of making pot and pearl ashes.

England had suffered bitterly from monopolies—monopolies based not on invention, but on royal pleasure. There had been granted to favorites of the English court monopolies covering ordinary articles of necessity and commerce, such as tea and salt. Exorbitant profits had been exacted from the English public, and the privileges so greatly abused as to become, finally, unbearable. In 1623 the statute of James was enacted, abolishing all English monopolies except such as were founded on invention. The latter were recognized as lawful and as conducing to the good of England by stimulating new trade and industries. The value of such monopolies is well expressed in the decision of an old English court, as follows:

"But if a man hath brought in a new invention and a new trade within the kingdom, in peril of his life and consumption

of his estate and stock, etc., or if a man hath made a new discovery of anything, in such cases the king of his grace and favor, in recompense of his costs and travail, may grant by charter unto him, that he only shall use such a trade or traffic for a certain time, because at first the people of the kingdom are ignorant and have not the knowledge or skill to use it. But when that patent is expired, the king cannot make a new grant thereof, for when the trade is become common, and others have been bound apprentices to the same trade, there is no reason that such should be forbidden to use it."

We see, then, that our forefathers merely followed British precedent in providing for exclusive grants to authors and inventors.

During the first year of our patent history, only three patents were granted. Even ten years later the entire routine of the patent system was carried on by a single clerk. But conditions finally improved, and about 1801 a clerk and messenger were added to the staff, also a pony on which the messenger could ride when taking the papers to the State Department for the signature of the Secretary.

All this seems very simple and primitive to us, but we should remember that science was then but awakening. Volta's battery had just been given to the world, and Galvani's book on animal electricity was only about ten years old.

We are told that when the British invaded Washington, during the War of 1812, burning Government buildings and supplies, the old patent office was saved only by the patriotism of Dr. William Thornton, the able scientist then in charge. It is said that when the British approached to burn the buildings, he appeared on the portico and cried:

"This is the emporium of the arts and sciences of America; don't burn it."

At all events, the building was spared. However, in 1836, after 10,000 patents had been issued, the building caught fire, and was totally destroyed, together with all its contents of records, books and models.

During this same year, the patent statutes were completely readjusted, and the patent system became essentially what it is to-day. Provision was made for the appointment of a Commis-

sioner of Patents and also for a corps of experts to examine into the novelty of alleged inventions. This was the real beginning of the search system which has for many years distinguished the American patent system from all others, searches to prevent the grant of patents for things not really new.

The importance of such searches into the prior art was quickly appreciated, and has ever remained the keynote of the American system.

Each issued patent bears evidence that it has been compared with all others and has been found to possess some features of novelty. In some cases, the novelty over the prior art is small, in other cases, great; but in all cases, the novel features are pointed out in the claims of the patent in such terms that all persons skilled in the art may know what the inventor has really contributed to the progress of science and the useful arts.

Patent claims are not, as a rule, easy reading, for, being part of a contract, they are necessarily somewhat formal.

The contractual relation between the inventor and the people of the United States arises from the circumstance that the inventor has something to sell which the public desires to buy. The inventor has knowledge enabling him to attain some desired result in a new or better way, and is willing to impart that information to others for an adequate consideration. The people of the United States desire to make use of the inventor's new idea, and therefore buy it, paying for it not in money, but in a monopoly for a limited period. The patent specification indicates the nature of the bargain. The description and drawing show how the inventor's new idea can be used to promote the progress of science and the useful arts, while the claims point out the limits of the monopoly granted in exchange. In this way, the people learn of new arts, machines, manufactures and compositions of matter which otherwise would be concealed from them, while the inventor receives adequate reward for his genius.

That the American patent system has been successful in fostering new industries is evidenced by the large and increasing number of patents issued each week. It is also shown by the successful development of many new industries, which, but for the protection of patents, could never have survived the

struggles and expense of early existence. In the electrochemical arts especially, these new industries are prominent.

The patent office is a sensitive barometer of our manufactures. Activity in any particular art is almost invariably indicated by an increase in the number of patents granted in that art. If we go to war, there is a flood of patents on war supplies. If we have a coal strike, the patent office is besieged by applicants with new types of crude oil burners. Year by year, the needs of the country change, but the inventor is always on hand to supply those needs and reap his reward.

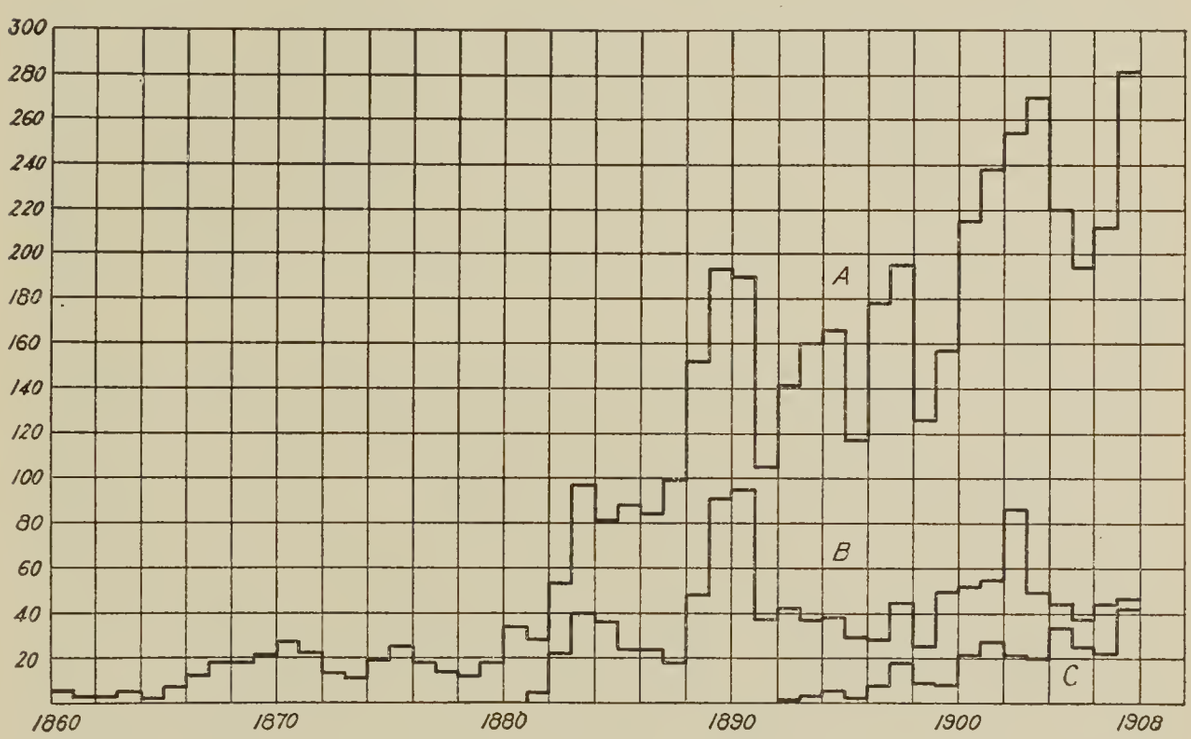


FIG. 1.

In the electrocheimcal arts, the developments have, in the last few years, been rapid, indeed. This can be graphically shown by reference to the accompanying diagrams or curves, in which, as abscissa, we have years, and as ordinates, the number of patents granted for the year.

The uppermost curve, Curve A, shows all the electrochemical patents from 1860 to date, and indicates most clearly how rapid has been the development.

The curve points to new arts, new machines, new manufactures, and new compositions of matter, all undiscovered and all holding out the promise of exclusive use to anyone clever and industrious enough to find them.

By resolving this curve into its components, we can see in what departments of electrochemistry development is now most rapid. Only two sub-classes are here shown, but these are typical and serve to show the intimate relation between the patent system and the country's industries.

Curve B represents patents on secondary batteries, and Curve C, those on electric furnaces. The storage battery art started about 1882, and reached a maximum in 1890. Then came a period of depression, which lasted until the advent of the nickel battery, about 1902.

The electric furnace art is still in its infancy. Almost the entire list of furnace patents are still within the monopolistic period of seventeen years. Each day that period moves forward one notch, bringing to a close some inventor's monopoly, and releasing to public use the fruits of the inventor's genius. The debt to the inventor has been paid in full, and the public comes into its own.

This plan of paying debts to inventors is, in many respects, admirable. If the inventor's new scheme has proved inoperative or otherwise worthless, no one has cared to use it and the inventor's monopoly has netted him nothing. If the new scheme has filled a great need, then the public has gladly paid the license fee, and the inventor's profits have been large. The system is thus largely automatic, providing little payments for little improvements and big payments for big improvements.

In some instances, the inventor's monopoly seems a burden to the public. If, however, the people do not care to take advantage of the inventor's skill, they need not do so. If they prefer to cling to old methods and apparatus, rather than pay the royalties demanded by the inventor for use of his improvements, they may. Though the public have contracted with the inventor to the extent of giving him a monopoly on his new idea, there is no guarantee that the new idea will ever be used sufficiently to give value to the monopoly. The inventor must rely on his own judgment as to the money value of his monopoly.

Since the patent specification is in the nature of a contract between the inventor and the public, the specification must be drawn with care. If the inventor offers something not really new, then the offer must be refused by the public. If he demands

a monopoly broader than his invention, then also must he be refused. But when the new idea marks a real advancement in the art, and is offered in exchange for a monopoly of equal scope, then is there opportunity for a bargain between inventor and public.

Throughout the negotiations for a patent, the inventor is represented by his patent attorney, while the public interests are guarded by the Commissioner of Patents and his corps of experts or examiners. The attorney co-operates with the examiner in framing a patent specification fully expressive of the relative rights of the inventor and the public. This work is often long and laborious, and worthy of the best skill of both attorney and examiner. It is not a field for amateurs, either on one side or the other.

The negotiations are conducted according to various Rules of Practice, rules which experience has shown are necessary to an orderly consideration of the business of the patent office. The inventor pays certain fees to defray the expense of the negotiations and to provide for printing the patent, so that copies may be sent broadcast to make the new idea readily accessible to the public.

Sometimes the negotiations between the patent attorney and the Government expert, or examiner, drag on for years and develop into veritable contests, both as to scientific facts and as to legal principles. As a noted judge has said, the record becomes filled with "tentative debates between urgent and vociferous attorneys and reluctant and laconic examiners."

The attorney argues, but the examiner decides. In the main, he decides correctly, even though the problem submitted to him sometimes may be of the most intricate nature.

The examining corps of the patent office numbers about 300 men. Their duties are so largely judicial and require such broad training, in both science and law, that the personnel of the corps is of vital importance. For many years the country has been fortunate in this respect. The examiners have been technical graduates, and with few exceptions, members of the bar. Considering the arduous nature of an examiner's duties and the pitifully small salary paid for the service, the inventors and the public are to be congratulated on the success with which the patent office force has been recruited and maintained.

For years there has been an ever-increasing burden of work, with little or no increase in force. For years the cost of living has increased, with no change in patent office salaries. The examining corps has struggled on as best it could under the overload, getting small honor for faithful work, and from slighted inventors, "curses, not loud, but deep."

If an examiner was unable or unwilling to stand the strain of overwork, he could resign. If he felt underpaid, he could go elsewhere. And this is exactly what the examiners have done. Out of a corps of 300, 135 have resigned within a period of less than five years.

For every resignation of an experienced examiner, a new man has, of necessity, been sought out and broken to the work, all of which has taken time and patience on the part of the older men.

We have but to read the last report of the Commissioner of Patents to realize that this condition cannot long continue. He has, in no uncertain terms, pointed out the needs of his office, and indicated to Congress how, in his opinion, those needs can best be met.

The Patent Law Association, a representative body of patent attorneys, has for several years used its influence for the betterment of conditions in the patent office. Much has been accomplished, but much still remains undone.

Unfortunately, however, the inventors and manufacturers of the country have not been alive to the needs of the system which has proved so beneficial to the country's industries. Is it not time for these men to lend a hand in relieving the overcrowded condition of the patent office and in seeing that some of the more pressing needs are supplied?

Probably not all inventors know what the real conditions are nor how to find out, and with this as an excuse, the following quotation is made from the last report of the Commissioner of Patents to the Secretary of the Interior. I quote:

CONDITION OF WORK.

"The work has been for years very much in arrears, and is in the same condition at this time. This has been found to be caused, first, mainly by the insufficient force of examiners and clerks to meet the great volume of work coming in, a large

increase yearly, which yearly increase is not always capable of being estimated in advance, so that the same arrearage of work has existed each year for many years. The examining corps of the office has repeatedly worked until 5 o'clock, even when the official day closed at 4 o'clock, for many years, and they have been called upon several times to work later than this hour, and have frequently forfeited a part or all of their annual leaves for the purpose of bringing up their work, in order that a good showing might be made before Congress met. Their efforts under these conditions were at best spasmodic, and simply resulted in thousands of actions being made which were nothing more than frivolous. After one of these annual efforts, it was necessary to do a greater portion of that work all over again, and it really had the effect of throwing the business of examination of applications further back than ever. This resulted not only in vexatious delays to the inventors, but it caused hundreds of complaints to be filed, and what was still more embarrassing and serious, a great many applications were passed to issue that were not ready for patent, with the result that the inventors and owners of meritorious inventions forfeited valuable rights by these careless, ill-considered and hasty actions on the part of the office. The inventors are entitled to be protected, as well as the public, and they should always be helped by the office in all legitimate ways. The inventors pay the Government for the work to be done in the examination and issue of their patents, even though they appeal their cases in regular order to all the tribunals of this office and finally to the United States Court of Appeals of the District of Columbia, for a fee is charged for each appeal, in addition to the Government fee of $35. Complaints against the conduct of affairs in this office have been numerous, and many have been based upon good and sufficient grounds. The affairs of the office should be so conducted that very few, if any, just complaints could be lodged. In view, therefore, of the great amount of accumulated work and the great volume of work that is constantly coming in, increasing each year and keeping pace with the growth of the country and the activities of manufactures and commerce, I am most decidedly of the opinion that the present force cannot cope with it. I have, therefore, after a most careful investigation of the office

needs in this respect, asked for a sufficient number of examiners and clerks to bring the arrearages up to date and to dispose of the great amount of incoming work material. If the force asked for be granted and made immediately available, I believe that the accumulated work can be disposed of, and that it will be possible in the future for the average inventor's application to be acted upon, either rejected or a patent allowed, within thirty days of its receipt. The inventors are entitled to prompt action, and they should be accorded it."

The commissioner's statements, above quoted, are perfectly plain. He admits the vexatious delays and hasty office actions, and clearly states facts well known to attorneys practicing before the office.

Now, where lies the responsibility for these conditions? Clearly, they are not due to lack of funds, for the patent office has a yearly surplus of nearly $300,000, and a total surplus of something like $6,000,000—all of it money taken from inventors and manufacturers in the form of fees. In its final analysis, the whole responsibility for the undesirable condition of affairs comes back to the inventors and manufacturers. So long as they are content to smother with work a half-paid examining force, depleted by resignations and demoralized by raw recruits, just so long will inventors' applications be slighted and inventors' letters go for months unanswered.

It is true that Congress alone can change the patent office organization and the salaries of the examiners, but in matters of this kind Congress is not deaf to the needs of the country. Inventors and manufacturers, once informed of true conditions and proper remedies, could effect speedy relief and permanent improvement. The patent office business is in reality their business, and the patent office needs, their needs.

Let me plead, then, for more interest in patent office affairs and patent office needs. Not in the form of disgruntled outbursts through the public press, for of those we have had enough and to spare, but instead, fair criticism and kindly suggestion based on intelligent understanding. After the more pressing needs are supplied, there will be ample time to consider the half-baked schemes with which the technical periodicals have recently been flooded. To those of you who are teachers, let me suggest that

you give your students some knowledge of the relation between inventors and the public. Why not offer courses in patent law; not for purposes of developing patent solicitors, but solely for the purpose of instilling in the student's mind some of the fundamental conceptions of our present patent system? Sooner or later, the average technical graduate is confronted by a patent situation of some importance. The greater his knowledge of patents, the greater his ability to guide his business to safety. No man can profitably be his own lawyer, but many a business man suffers great financial loss solely by failure to recognize some fundamental principle of the law of patents. To those of this society whose genius creates new arts and to those who place at our doors the fruits of those arts, let me plead for an active participation in the movement to improve the affairs of the patent office. You know the far-reaching benefit of the patent system and you are in a most advantageous position to assist the commissioner in his efforts to improve it.

You are business men and appreciate the advantage of efficient methods. In your own affairs, you supply all needed facilities, and then demand promptness and accuracy. Why should you not see that the same principle is applied to patent office business, which, after all, is but another branch of your own business? You have neglected it for a long time, but can you afford to do so longer?

Your Congressman is, of course, the medium through which a more intimate knowledge may be gained, also the medium through which your views can be expressed. On you devolves the duty of seeing what is needed, and on him, the duty of seeing those needs supplied.

Our forefathers gave Congress power "to promote the progress of Science and Useful Arts." But that was long ago, and Congress soon forgets.

DISCUSSION.

Mr. Louis C. Raegener: It seems to me what we want more than a reform in the Patent Office, is a reform of the patent laws generally.

After an active practice of thirty years in the Federal courts I have come to the conclusion that our patent laws are made for the special benefit of patent lawyers and infringers.

Every patent law suit costs an unconscionable amount of money and usually takes several years to try. It is a waste of time and money to attempt to obtain a money judgment for damages. The amount awarded is always inadequate and seldom recoverable. The fees paid by a successful plaintiff to his lawyer and expert are not taxable and are not recoverable.

But there is another aspect of the absurd condition of our patent laws. I dare say that most of you here present do not realize that. Twenty-five years ago or more a decision in a patent suit rendered by the Circuit Court was appealed to the Supreme Court of the United States, and when the Supreme Court of the United States finally disposed of the question and sustained the patent, that patent was valid from the Atlantic to the Pacific and the patentee possessed a real monopoly.

Because the Supreme Court was supposed to be overburdened with work and for the purpose of speeding appeals, nine Circuit Courts of Appeals were created and appeals to the United States Supreme Court were no longer permitted.

The patent laws are supposed to protect the inventor throughout the United States. As a matter of fact, the United States is divided into nine different countries, for all practical purposes, as far as patents are concerned, and a patentee might just as well file his patent in these nine different countries and be prepared for nine different and conflicting opinions from each of the nine Circuit Courts of Appeals. A plaintiff, after spending a fortune in having his patent sustained by one of the Circuit Courts of Appeals, finds a new infringer in another Circuit. The decision which was rendered by the Courts of first resort—final so far as he can control matters—is treated with no respect outside of its jurisdictional limits, and the owner of a so-called monopoly must begin his litigation all over again in another Circuit Court and

again lose several years in trying the case, and finally learn that on identically the same facts the learned Circuit Court of Appeals is reluctantly forced to reach a diametrically opposite conclusion to that reached by the Circuit Court of Appeals which first heard the case.

Now, the unfortunate plaintiff can petition the Supreme Court of the United States to hear such a case, and if the Supreme Court of the United States is not too busy and considers the matter of sufficient importance, then after the expiration of another year or so a final decision is rendered declaring such a patent valid or invalid.

It is hardly conceivable that such an absurd system could exist for ten or fifteen years, and the Government not remedy it.

Dr. H. N. Potter: I have had a slight experience with the American office and the German office, and I wish to suggest that much of our troubles come from the fact that our patent dates from the date of issue instead of the date of the application. The interference begins with date of conception. The German office says in effect that if a man wants something he can come and get it, and the first one in, barring theft of the idea, has the right of priority. This eliminates all interference, troubles and delays. The patent runs from date of application, and any subsequent litigation does not affect the period of the patent. Therefore, the patent attorney has no object in procrastination.

Mr. Raegener: The German law, in my opinion, is far superior to ours, for it gives actual protection to the patentee.

If anyone is aggrieved by the issue of what he believes to be an invalid patent, he can begin proceedings in the German Patent Office to vacate such a patent; but until such a patent is vacated by the Patent Office it must be respected and an infringer is liable to imprisonment for infringement.

Again, if a patent has not been assailed in the Patent Office after the expiration of five years, it is practically unassailable and most of the ordinary defences against patents are no longer available to an infringer.

Dr. C. P. Steinmetz: There are undoubtedly some patent laws of other nations, I think, for instance, the German, which give better protection to the *patentee,* but I doubt whether that is the condition which we want. The condition which we are after

is to give better protection to the *inventor,* and there is a difference between the patentee and the inventor in many countries, where the first one who comes to the patent office gets the patent, and that excludes in many cases the inventor from getting the patent.

Mr. L. H. Baekeland: As far as my own experience goes, I know that patents seldom help to protect the inventor because the inventor himself is not usually a rich man and can hardly afford to spend the enormous sums of money required for maintaining his rights. I know of several cases where an invention has simply been good for maintaining a monopoly of a rich corporation to the detriment of the public and to no advantage to the inventor. I know of one particular instance where a rich company maintains an expensive staff of lawyers and pays its chemists very poorly. In that company the regular proceedure is, whenever an inventor comes around and wants to sell a patent, he usually starts in by asking the traditional "millions," then comes down to one hundred thousand dollars, or perhaps ten thousand dollars, and after talking with the lawyers of this company for a few minutes longer, he is willing to take one thousand dollars. They say to him—you will take one thousand dollars or we will spend one hundred thousand dollars to defeat your patent. The inventor walks in with a great deal of self-assurance and somehow or other he walks out with a feeling as if he had committed some very serious crime in obtaining a patent.

I know of another case where a man had invented a very useful improvement, and another man was eager to the utmost to utilize that improvement, and obtain a license, and everything went along smoothly until the moment when a lawyer began to draw up the papers and made matters so difficult and complicated that nothing came out of it. The patent is still unused.

Mr. A. B. Marvin, Jr: If you care to find out more about the movement for the establishment of a Court of Patent Appeals, you can do so by writing your Congressman for a copy of the bill now pending. If you want to find out why it is that a German patent is in many respects stronger than an American patent, you should remember that the German Patent Office has a staff much larger than that of our Patent Office, and that the Germans grant fewer patents. The result is that when an application comes in

for examination it is immediately taken up and carefully considered. Such prompt action is impossible in this country, because of the lack of examiners. So long as these conditions hold we must expect many patents weak enough to be defeated in the courts—patents which are not strong, for the simple reason that they could not be carefully considered in the office.

I would suggest that all this matter has been brought before Congress at the present session, and if you are sufficiently interested you can easily get in touch with it through your Congressman. I hope my paper has started some thought along this line.

Mr. A. B. Marvin, Jr. *(communicated):* Since the above paper was delivered, Congress has passed a bill providing for a material increase in the staff of the Patent Office, and in the salaries paid examiners. This bill went into effect July 1st, and will enable the Commissioner of Patents to carry out those improvements in Patent Office affairs for which he has so long and persistently fought.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 1, 1908. President C. F. Burgess in the Chair.

THE LATENT HEAT OF VAPORIZATION OF METALS AND OTHER SUBSTANCES.

By Joseph W. Richards.

Although the subject of this paper is not strictly electrochemical, yet electrochemists often have a great deal to do with it. In electric furnace operations if carried out for the purpose of reducing and distilling zinc, cadmium, mercury, sodium, potassium or other volatile metals from their ores, the latent heat contained in the vapors of these metals is a large item in the total energy concerned in the process. When local temperatures in electric furnaces become too high, and the working zone too restricted, we are accustomed to say that electric energy is wasted in useless vaporization of substances at the high temperature produced, but the quantitative side of this phenomenon has been almost entirely unknown.

I hope by this discussion to throw a little light on this matter, in its quantitative aspect, and thus to increase the exact knowledge of "what is going on" in electric furnaces.

From the lecture of Dr. Steinmetz preceding this paper, and the discussion thereupon, we see some simple relations between the specific heats of substances, when expressed per molecular weight. Dulong and Petit were really the first in this field, when setting forth the familiar observation, to be found in every elementary treatise on chemistry or physics, that atomic weight times specific heat is a constant, averaging about 6.4. There are two things about this rule which are not usually mentioned, but they should be very carefully considered in every thorough study of the subject. First, the specific heats all increase with rising temperature, and the rule has been deduced by considering only the specific heats between 0° and 100°. Near to their melting points, the solid metals have specific heats 50 to 100 per cent.

greater, and the rule does not hold. Second, the atomic specific heat being nearly constant shows that in metals at ordinary temperature the moving particle whose motion constitutes heat energy is either the atom, or is the same multiple of the atom for all metals.

The writer has calculated the probable value of the Dulong and Petit constant, from the most reliable data, for the common metals, and finds it to be 6 at the absolute zero (—273° C) and 10 at the melting point of the metals. The mean, between —273 and 0° is about 6.2 or $6.2 \times 273 = 1693$ calories is required to raise atomic weight from absolute zero to the centigrade zero. The mean value of the atomic specific heat from absolute zero to the melting point T (equals centigrade melting point, t, plus 273°), is 8 calories, and the total heat in the solid metal at its melting point is 8 T calories.

The latent heat of fusion of atomic weight of a metal was first shown by the writer to be a function of the absolute temperature of the melting point (Journal of the Franklin Institute, May, 1897), and to be approximately 2 T. The total heat in melted metal at the melting point, counting again from absolute zero, will be $8\,T + 2\,T = 10\,T$ calories.

The specific heat of liquid metals is nearly constant, and equal to the specific heat of the solid metal at the melting point. This would make the atomic specific heat of the liquid metals approximately 10 calories. The heat required to raise the liquid metal from the melting to the boiling point from T absolute to T^1 absolute, is then $10\,(T^1 - T)$, and the total heat in the liquid metal at the boiling point, summing up again from absolute zero, is

$$10\,T + 10\,(T^1 - T) = 10\,T^1$$

The heat absorbed in volatilizing a substance is a function of the absolute temperature of the boiling point, T^1. Considering only the normal boiling point, that is, under atmospheric pressure of 760 m. m. mercury column, Trouton first showed that the latent heat of vaporization for molecular weight in grams is approximately 23 times the temperature, or $23\,T^1$, at constant atmospheric pressure. This constant refers to the molecule of the substance, that quantity whose motion constitutes temperature energy, and the constant is true only for the arbitrary pres-

sure named, being larger for lower temperatures and pressures and smaller for higher ones, until it reaches zero at the critical pressure.

Adding 23 T^1 to 10 T^1 we have 33 T^1 as the total heat in molecular weight of the metal as vapor at its normal boiling point, reckoning from absolute zero. If we wish to reckon from 0° C, we have 33 T^1 — 1700, as already explained.

EXPERIMENTAL DATA.

The actual latent heat of vaporization of but few metals is known; in fact, even the normal boiling points of most of them are either unknown or merely conjectured. As far as the author can discover, the latent heat of vaporization of mercury 67.8 calories per gram, is the only one which has been directly determined. This amounts to 13,560 calories per atomic (or molecular) weight of the vapor, and since the boiling point is 357° C = 630° absolute, the Trouton constant in this case is 13,560 ÷ 630 = 21.5.

APPROXIMATE VALUES FOR THE METALS.

Taking the best known values of the normal boiling points, we will construct a table of the probable values of the latent heat of vaporization, under constant pressure, of atomic weight of the metals.

Metal	At Wt.	B. P. C°.	B. P. T′	23 T′	L. H. Vap. per 1 kg.	33 T′ —1700	Total Heat in 1 kg. Vapor to 0° C.
Hg	200	357	630	14,490	72.5	19,090	95.5
K	39	720	993	22,840	586	31,070	797
Cd	106	778	1051	24,170	228	33,000	311
Na	23	900	1173	26,980	1173	37,000	1609
Zn	65	930	1203	27,670	426	38,000	585
In	. .	1000	1273	29,280	. .	40,300	. .
Mg	24	1100	1373	31,580	1316	43,600	1817
Te	127	1390	1663	38,250	301	54,880	432
Bi	208	1435	1708	39,280	189	56,360	271
Sb	120	1600	1873	43,080	359	60,110	509
Tl	204	1700	1973	45,380	222	63,410	311
Pb	207	1800	2073	47,680	230	66,710	324
Ag	108	2040	2313	53,200	493	74,630	691
Cu	63.5	2100	2373	54,580	860	76,610	1206
Sn	118	2170	2440	56,120	476	78,820	668
Mn	55	2200	2473	56,480	1027	79,510	1445
Ni	59	2325	2598	59,750	1013	84,030	1424
Cr	52	2365	2638	60,670	1167	85,350	1641
Fe	56	2420	2693	61,940	1106	87,170	1555
Pt	197	2450	2723	62,630	318	88,160	447
Ti	48	2475	2748	63,200	1317	88,980	1854
Rh	103	2500	2773	63,780	619	89,810	872
Ru	102	2515	2788	64,120	629	90,300	883
Au	197	2530	2803	64,470	327	90,800	461
Pd	106.5	2535	2808	64,580	606	90,960	854
Ir	193	2545	2818	64,810	336	91,290	473
Os	191	2600	2873	66 080	346	93,110	487
U	239	2900	3173	72,980	305	103,010	431
Mo	96	3200	3473	79,880	832	112,910	1176
W	184	3700	3973	91,380	497	129,410	703

DATA FOR NON-METALS.

The boiling points of a number of the non-metals are known, but in many cases the molecular formula at the boiling point is either unknown or doubtful.

To take some examples, we will calculate the vaporization to H^2, N^2, O^2, Cl^2, Br^2, I^3, P^3, As^3, Se^3, B^2, C^2.

Formula	Molecular Weight	B. P. C°	B. P. T′	23 T′	L. H. Vap. per 1 kg.	Experimentally Determined
H^2	2	—253	20	460	230	. .
N^2	28	—196	77	1,771	63	50
O^2	32	—188	85	1,955	61	58
Cl^2	71	—22	251	5,773	81	67
Br^2	160	58	331	7,613	48	46
I^3	381	174	447	10,280	27	24
P^3	93	287	560	12,880	138	130
As^3	225	450	723	16,629	74	. .
Se^3	237	690	963	22,150	94	. .
B^2	22	3700	3973	91,380	4.154	. .
C^2	24	3700	3973	91,380	3.808	. .

Such deviations from the rule show that many vapors, when saturated, are complexes, consisting of molecular mixtures of various kinds which simplify as the temperature rises.

As far as "other substances" are concerned, it is found that some give the Trouton constant over 23, at their normal boiling point, and some give less. In the absence of experimentally determined data, however, we should not hesitate to take 23 T^1, where T^1 is the absolute temperature of the normal boiling point (760 m. m. pressure) as a satisfactory first approximation to the heat of vaporization of one molecular weight.

BIBLIOGRAPHY OF ELECTROCHEMISTRY AND ALLIED SUBJECTS.

By P. F. Mottelay.

Electro-chemistry properly starts from Nicholson and Carlisle, A. D. 1800[1], due account having naturally been taken of the investigations and discoveries of Beccaria (1772), of Cavendish, of Priestley, of Van Marum, of Paets van Troostwijk and Deiman (who wrote, in 1789, the letter to Mr. Jean Claude De Lamétherie announcing the decomposition of water into hydrogen and oxygen by frictional electricity)[2], of Galvani (1789-1792), of Ritter (who, in 1798, recognized the relation between chemical and electro-chemical phenomena)[3], and of Volta (who made "the immortal discovery" of the pile in 1799-1800). All of these precede the records, more particularly, of Cruikshank[4], Dr. Henry, Wollaston[5], Erman, Gautherot, Davy[6], Berzelius and Hisinger[7], Faraday, Brugnatelli, Grotthus[8], Clausius[9], Hittorf[10], Kohlrausch[11] and Arrhenius.

The compiler of this bibliography has arranged alphabetically

[1] Although electro-chemistry is usually dated from the experiments of Nicholson and Carlisle, April 30, 1800, the investigations of Professor Fabbroni, of Florence, in 1792, claim a much earlier place in the history of the science (Nicholson's Quarto Journal, Vol. IV, page 179). The discoveries of Cruikshank and Davy, however, were those which tended most to lay the foundation of electro-chemistry. (W. Sturgeon, "Scientific Researches," 1850), Kopp remarks (Geschichte der Chemie, 1844, Vol. II, page 330) that the investigations of Nicholson and Carlisle were "the *first* recognitions of galvanic electricity as a chemical agent." They made "the fundamental observation from which arose the science of electro-chemistry." (W. C. D. Whetham. Theory of Exper. Elec.).

[2] Gren's Journal der Physic, 1790, Vol. II, page 91.

[3] Beiträge zur nähern Kenntniss des Galvanismus, Jena, 1800, Vol. I, page 252.

[4] Nicholson's Journal, Vol. IV, page 187; Gilbert's Annalen, Vol. VII, page 91.

[5] Annals of Electricity, Vol. IX, page 518; Phil. Trans., 1801, page 427; Annales de Chimie et de Physique XVI, page 45.

[6] Gilbert's Annalen, Vol. VII, page 114, 1801; Bakerian Lecture for 1806; Phil. Trans., for 1807, Vol. I, pages 28-30.

[7] Annales de Chimie, Vol. LI, pages 167, 174, 1804.

[8] Annales de Chimie, Vol. LVIII, pages 10, 54, 64, 68; Vol. LXIII, pages 20, 34, and Vol. LXXXII, page 34. Various papers are to be found listed at page 306, Vol. I, of Gmelin's Handbook of Chemistry.

[9] Poggendorff's Annalen, Vol. CI, pages 338, 347.

[10] Ostwald's Klassiker, Nos. 21 and 22; Poggendorff's Annalen, Vols. 89, 98, 103, 106.

[11] Wiedemann's Annalen, Vol. VI, page I; Vol. XI, page 653; Vol. XXVI, page 161.

such original selections of leading works in different languages as are thought most likely to answer all reference purposes, containing, as many do, special bibliographical lists of their own to which attention has in every instance been duly called. Herein will be found the first exhaustive record, carefully made, of all references to electro-chemistry, electrolysis, electro-metallurgy and allied subjects, not only throughout the 564 valuable pages of the Ronalds Electrical Catalogue by Alfred J. Frost, but also in the Benjamin lists of electrical books at the U. S. Naval Academy, as well as in the catalogue of the Sur. Gen. U. S. Army, and, likewise, those traced through proof galleys of the *catalogue raisonné* now being prepared by Mr. W. D. Weaver for the Library of the American Institute of Electrical Engineers in New York City.

It is needless saying that the extracts and references appearing throughout the above named have been taken by Mr. Frost and others from the leading scientific publications of the world. Some of the selections which, at first sight, might appear unwise, perhaps mainly on account of their early date, are purposely inserted by reason of their extreme curiosity and rarity; others, as, for instance, in the case of batteries, furnaces, etc., because they are known to contain the results of able investigations from important sources which are, besides, by many preferably wanted in the original.

All these, carefully grouped together, cannot but prove useful, and would in the main suffice for all ordinary requirements, but, for the completion of special researches, it has been thought best to mention particularly the following additional publications which can all naturally be consulted to great advantage, viz.:

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The author will appreciate suggestions as to improving the above compilation. It constitutes Appendix I of his "Bibliographical History of Electricity and Magnetism," which will shortly appear in book form and which, under the caption of Chronology, appeared in part serially in four countries several years ago.

MEMOIR
ON THE METHODS OF TREATMENT OF SIMPLE AND COMPLEX ORES
OF
MOLYBDENUM, TUNGSTEN, URANIUM, VANADIUM

BY

GUSTAVE GIN

Part II.—Tungsten.

Translated by Jos. W. Richards and W. S. Landis.

This Memoir was awarded the Frenzel Prize by the American Electrochemical Society.

HISTORICAL.

The presence of an unknown earth in cassiterite was suspected by Croustedt in 1758.

Woulfe in 1779 observed that the action of an acid on pulverized scheelite gave a characteristic yellow reaction which he could not satisfactorily explain.

In 1781 Scheele having melted tungsten (really scheelite) with potassium carbonate and treated the fused mass with water, obtained a solution from which nitric acid in excess precipitated a yellow powder which he called tungstic acid.

In 1782 Bergmann repeated Scheele's experiment and confirmed his conclusions.

Two of Bergmann's students, the d'Elhuyart brothers, Spanish chemists, recognized in 1783 the same combination in wolframite (etymology *froth of the wolf*). Reducing wolframite by carbon, they prepared a heavy metal, which they called tungsten, and made alloys of it with gold, silver and lead.

The preparation of tungsten by the reduction of tungstic acid by carbon was again taken up in 1791 by Ruprecht and Tondy, in 1794 by Vauquelin and Hecht, in 1813 by Allen and Aiken, in 1859 by Buchholz and by Hernouilli.

The compounds of tungsten were further studied by Davy, Wohler, Malaguti, Forcher, Riche, Roscoe, Berzelius, Margueritte, Laurent, Persoz, Marignac, Lefort, etc.

Since then much investigation has been done on new compounds of tungsten by Defaqz, Hallopeau, Pechard, Vigoroux, Delepine, Gin, Moissan, Feree, Williams, etc.

TECHNICAL COMPOUNDS OF TUNGSTEN.

Metallurgically, tungsten is used directly and indirectly either as pure tungsten or as compounds of tungsten with carbon, silicon, or metals of the iron family. Before taking up the manufacture of these various products we will describe their essential properties.

PURE TUNGSTEN.

Physical Properties.—These depend on the manner of its preparation. Reduction by hydrogen at dull redness gives an amorphous steel gray powder with a fine luster. The reduction of tungstic acid by potassium by Wohler's method gives a more brilliant powder with crystalline aspect.

By electrolyzing molten sodium tungstate Zettnow obtained the metal in the state of a black amorphous powder. It is pyrophoric when prepared according to Feree's method by using mercury as a cathode, forming an amalgam and then distilling off the mercury.

Tungsten is difficultly fusible, its melting point having been recently given as 2,800 to 3,000° C. When pure and porous, it can be welded by forging at a temperature of about 1,000° C. It can be drilled and filed easily and is not magnetic.

Its density is high and also depends on the method of preparation. It varies from 17 to 18 for the pulvurent varieties. Pure tungsten melted in the electric furnace has a density of 18.7. Heated to 1,000° C. and compressed under a pressure of 200 kilograms per square centimeter (200 atmospheres) gives a density as high as 18.92. Its specific heat is about 0.034 at 0° C., and increases with the temperature. Its electrical resistivity as deter-

mined by the author is 86×10^{-6} ($= 0.000086$) ohms per $\frac{\text{cm}}{\text{cm}}$ at 20° C.

Chemical Properties.—Tungsten is attacked by fluorine at ordinary temperatures with intumescence, forming a volatile fluoride. Dry chlorine attacks it at about 300° C., forming the hexachloride; moist chlorine gas forms the red oxychloride. Bromine acts on it only at low redness, forming the pentabromide; iodine attacks it only at a bright cherry red.

Oxygen, either dry or moist, has only a feeble action on it at ordinary temperatures; however the metal blackens little by little in the air. At redness tungsten is attacked by oxygen, forming tungstic acid; it burns likewise in air at bright redness, swelling up and forming a powdery mass of tungstic acid.

Melted sulphur transforms it slowly into sulphide.

Nitrogen has no action at redness; the vapor of phosphorus attacks powdered tungsten at redness. In the electric furnace carbon, boron and silicon unite to form carbides, borides and silicides.

Tungsten is not sensibly attacked by water at ordinary temperatures; it is rapidly by vapor of water at redness.

Hydrofluoric and sulphuric acids attack it slowly; nitric acid and aqua regia transform it into tungstic acid. Carbon bi-sulphide and hydrogen sulphide attack tungsten at redness, forming the bi-sulphide. Several fused oxidizing agents, such as lead peroxide and potassium chlorate, attack the powdered metal with incandescence. Fused sodium carbonate and the alkalies dissolve it slowly. A mixture of carbonate and nitrate of potassium oxidizes it rapidly, forming potassium tungstate.

Tungsten reduces the alkaline sulphates to tungstates.

Arsenide of tungsten heated with copper out of contact with air up to the melting point of copper is completely decomposed, forming copper arsenide and metallic tungsten. It is the same with arsenide of copper when the latter contains less than 20 per cent. of arsenic.

COMPOUNDS OF TUNGSTEN AND BORON.

The binary compound of tungsten and boron is the only one which has been studied; formula WB_2; discovered by Tucker and Moody.

A mixture of boron and tungsten heated in the electric furnace gives a metallic compound crystalline in appearance and sufficiently hard to scratch the ruby easily. It crystallizes in octahedrons, microscopic in size, and has a density of 9.6. Dilute and concentrated acids do not attack it; aqua regia, on the contrary, attacks it easily.

COMPOUNDS OF TUNGSTEN AND CARBON.

Two carbides are known—W_2C and WC.

W_2C was discovered by Moissan who prepared it by heating in the electric furnace a mixture of tungstic anhydride with an excess of sugar carbon. It is iron gray in color and very hard, scratching corundum easily. Density at 18° C. 16.06. It gives almost the same reactions as metallic tungsten, but is more easily attacked by reagents. It takes fire in cold fluorine, in chlorine at 500° C. and in oxygen at 500° C. Gaseous or dissolved non-oxygen containing acids attack it very slowly; nitric acid on boiling dissolves it rapidly. When molten it can dissolve up to 8 per cent. of its weight of carbon, which separates out on cooling in the form of graphite. Potassium chlorate and a mixture of potassium carbonate and nitrate oxidize it with bright incandescence.

The carbide WC was discovered by Williams, who prepared it by heating in a forge fire to a high temperature a mixture of 120 part of tungstic anhydride, 20 parts of petroleum coke and 150 parts of iron in a carbon lined crucible. On cooling a metallic appearing button was found in the crucible, well fused, fairly hard, crystalline, and containing the carbide WC, iron in excess, and a double carbide of iron and tungsten. Acting upon it with hydrochloric acid, the iron was dissolved and the double carbide was separated from the residue by means of a magnet, leaving the carbide WC. The same method of preparation can be used in the electric furnace.

The carbide WC is an iron gray powder, consisting of microscopic opaque cubes; is hard, easily scratching quartz; density at 18° C. 15.7. It fuses very difficultly. A small quantity placed in a crucible of retort carbon, well closed, was heated fifteen minutes by a current of 950 amperes at 45 volts. The carbide was partially fused and transformed into W_2C and graphite as was proven

by the analysis of the molten parts. Heated to redness in a current of dry hydrogen, it was unaltered. Heated in the presence of air or oxygen, it oxidizes slowly, forming tungstic acid and carbonic acid.

Nitrogen is without action upon it at redness. Fluorine attacks it cold with incandescence; chlorine, bromine and iodine are entirely without action upon it even at bright redness. Non-oxygen containing acids, either gaseous or in solution, do not attack it. Heated with hydrochloric acid in a sealed tube for three hours at 350° C. did not attack it, although a considerable quantity of sodium chloride crystals separated out on cooling, coming from the glass of the tube.

Nitric and sulphuric acids attack it very slowly. Water does not act upon it up to the temperature of softening of Bohemian glass. It is oxidized easily on heated with chlorate or nitrate of potassium; bi-sulphate and carbonate of potassium attack it only slightly.

COMPOUNDS OF TUNGSTEN WITH SILICON.

The compound W_2Si_3 is known and the existence WSi is suspected. W_2Si_3 was obtained by Moissan in the electric furnace by mixing silicon and tungsten. It is a metallic substance, crystalline and hard enough to scratch the ruby. Vigoroux isolated it by taking the ingot obtained in the electric furnace and suspending it in a solution of hydrochloric acid, making it an anode against a carbon cathode. Using a direct current, the metal was dissolved and the silicide remained almost intact. The residual crystals were collected, treated with aqua regia, then with ammonia and finally with hydrofluoric acid. The silicide of carbon was then removed by its lower specific gravity, using methyl iodide for this purpose. It forms fine crystals in the form of metallic plates of a steel gray color. They are rather heavy, having a density of 10.9 and are fusible at about 1,400° C. Dry chlorine attacks them with vivid incandescence between 200 and 300° C., forming silicon chloride and tungsten chloride which deposits in the tube. Bromine forms a bromide below redness and without incandescence which condenses a little beyond the point heated. Iodine forms an iodide above redness, without incandescence. Pure dry oxygen burns it towards 500° C. with vivid incandescence; dry

air oxidizes it below redness without incandescence. Nitrogen does not attack it at any temperature.

Hydrochloric, hydrofluoric, nitric acids, etc., have no action, hot or cold. Gaseous hydrochloric acid does not attack it even at the temperature of the Bunsen flame. Aqua regia, even hot, has inappreciable effect. A mixture of nitric and hydrofluoric acids acts on it violently, even when cold, with the disengagement of abundant vapors.

Alkalies in solution attack it slightly, when fused their action is very strong. Fused alkaline carbonates form alkali silicate and tungstate with incandescence. Potassium nitrate acts less violently.

The silicide WSi contains a little more than 13 per cent. of silicon and probably exists. At least I have obtained in the electric furnace a crystalline product of this composition appearing to be a definite compound. It has not been studied further.

COMBINATIONS OF TUNGSTEN WITH THE METALS.

ALLOYS OF TUNGSTEN AND ALUMINUM.

By pouring liquid aluminium upon tungstic acid, Moissan prepared several alloys of aluminium and tungsten. He prepared them likewise by the ordinary alumino-thermic method. W_2Al may be prepared by the Goldschmidt alumino-thermic process. It forms brilliant crystals unattacked by acids or aqua regia.

WAl_3 is prepared in a similar manner; is likewise crystalline and unattacked by acids.

WAl_4 was prepared by Wohler and Michel by melting together at redness tungsten anhydride, cryolite, sodium chloride and potassium. It is in the form of orthorhombic prisms, density 5.58, easily attacked by nitric and other concentrated acids.

ALLOYS OF TUNGSTEN AND NICKEL.

The alloys of nickel and tungsten may be prepared by alumino-thermy or by the reaction of the silicides of nickel on tungstic acid. By reducing a mixture of NiO and WO_2 by alumino-thermy I have obtained nickel-tungsten alloys with a varying content of nickel.

WNi_2 crystallizes in serrated plates of a silvery white color, density 14.4 and is magnetic.

W_2Ni_3 crystallizes in larger plates than the preceding and of a grayer color; it is non-magnetic or very slightly magnetic; density 14.8.

By acting upon WO_3 and WO_2 with Ni_2Si and NiSi, I have obtained alloys which possibly contain WNi_3 and WNi, but they have not been isolated nor specially studied. We will consider further on the industrial manufacture of alloys of tungsten and nickel.

FERRO-TUNGSTEN.

Tungsten alloys easily with iron and gives to steel very interesting properties which will be studied at length further on.

Bernouilli showed that when cast iron was heated with varying proportions of tungstic acid, very hard alloys were obtained; the ancient Damascus steels contained tungsten which was probably the cause of their peculiar properties.

Berthier obtained alloys of iron and tungsten in 1834; Captain Caron studied these alloys in 1868, and determined that the hardness and strength of the metal increased with the proportion of tungsten. In 1883 Osmond noted that tungsten raises the transformation points of iron. In 1893 Poleck and Grutzner recognized the existence of W_2Fe and W_3FeC_2. In 1897 Carnot and Goutal isolated W Fe_3 and Behrens found in 50 per cent. ferro-tungsten octahedrons of the composition WFe_2. In 1897 Morten analyzed a very hard alloy which gave the composition W_4Fe. In 1900 the author prepared WFe_3 by the reduction of tungstic acid by means of ferro-silicon. Finally Vigoroux by an alumino-thermic reaction isolated W_2Fe_3.

Altogether, the following compounds have been studied: W_2Fe, W_2Fe_3, WFe_2, WFe_3.

W_2Fe comes in silvery-white hexagonal crystals of the hardness 9; density 17, non-magnetic; attacked by fluorine at a low temperature and by chlorine at low redness; combines with oxygen directly at redness; the halogen acids attack very slightly or not at all; nitric acid and a mixture of nitric and hydrofluoric acids dissolve it readily; fused potassium nitrate and potassium chlorate attack the pulverized metal with incandescence.

W_2Fe_3 was obtained by Vigoroux by an alumino-thermic reaction in a magnesite crucible, using a mixture of iron oxide and of tungstic oxide prepared from pure ammonium tungstate. The

fused ingot was treated with hydrochloric acid to dissolve out the free iron. The alloy was obtained in brilliant plates with metallic luster; density 13.89; not sensibly magnetic. Chlorine attacks it very actively at 300° C., leaving no residue; dry oxygen oxidizes it only at bright redness; gaseous hydrochloric acid even at bright redness attacks it only feebly. Hydrochloric and nitric acids in solution have no sensible action. Aqua regia acts feebly, likewise sulphuric acid acts only when concentrated and boiling. Potassium bi-sulphate, at low redness attacks it rapidly; it is its best solvent. Potassium chlorate even at its decomposition point acts only slightly. Nitrogen attacks it at redness with incandescence. Alkaline carbonates disintegrate it at bright redness.

WFe_2 appears not to have been studied.

WFe_3 has been isolated as small metallic octahedral crystals of a silvery color; density 10.7; hardness 6. Its electrical resistance at 20° C. is 0.000034 ohns per $\overline{cm}^3$. It is magnetic. Chlorine attacks it at redness; oxygen and dry air have no action at ordinary temperatures, but attack it at low redness; likewise vapor of sulphur. The halogen acids in the gaseous state attack it, but much more easily when dissolved. Nitric acid dissolves it rapidly.

ALLOYS OF TUNGSTEN AND MANGANESE.

WMn. I have prepared this alloy by reducing in the electric furnace Hubnerite, $MnWO_4$, containing only 1 percent. of iron. It is in flat crystals with large facets, and of a grayish white color; density 9.63; hardness 7; not magnetic. It is attacked by chlorine at low redness; it burns in oxygen at redness; boiling sulphuric and nitric acids attack it easily.

ALLOYS OF TUNGSTEN AND CHROMIUM.

I have made in the electric furnace various compounds of chromium and tungsten, but which always have contained notable amounts of iron, manganese, silicon and carbon. These so masked their characteristic properties that I have not studied them out. Their manufacture will be described further on.

ALLOYS OF TUNGSTEN AND MOLYBDENUM.

Stavenhagen and Suchard have prepared, by using aluminium for the reduction of a mixture of the oxides of tungsten and

molydenum, WMo. I have obtained W_2Mo_3 by reducing MoO_2 by W_2Si_3:

$$W_2Si_3 + 3\ MoO_2 + 3\ CaO = 3\ CaSiO_3 + W_2Mo_3.$$

These alloys are a brilliant silver white, the crystals have large facets and are hard and very brittle. The alloy W_2Mo_3 has a density of 14.8.

ALLOYS OF TUNGSTEN AND LEAD.

The alloy WPb has been obtained by the d'Elhuhart brothers by heating lead and tungstic acid in the presence of carbon. It has been likewise prepared by the action of aluminium on a mixture of the oxides. I have obtained a compound which appears to be WPb_2 by electrolyzing the double chloride of tungsten and sodium, using a lead cathode. These alloys are foliated, brittle and the alloy WPb has a high melting point.

ALLOYS OF TUNGSTEN AND COPPER.

These alloys have been prepared by Bernouilli and by Perey. They are very difficult to obtain by direct fusion because of their high melting point. They are easily obtained by the use of aluminium and by the reaction of molten copper silicide on tungstic acid. These alloys do not seem to have any industrial interest.

THE TUNGSTEN MINERALS.

The usual occurrence of the metal in nature is as tungstic acid or as a tungstate. It is frequently accompanied by tin minerals.

The principal minerals are:

Tungstite or Wolframine, WO_3.
Scheelite, $CaWO_4$.
Wolframite, $(Fe, Mn)WO_4$.
Hubnerite, $MnWO_4$.
Stolzite, $PbWO_4$.
Cuproscheelite, $CuCa_2(WO_4)_3$.

Tungstite (Syn. Wolframine, Wolframochre) WO_3. It is a pulvurent tungstic acid of a clear, yellow or greenish-yellow color and accompanies wolframite in the mines of Cumberland and Cornwall, Monroe, St. Leonard near Limoges, and at Meymac in Correze. It is soluble in alkalies, insoluble in acids; with salt of

phosphorus in the reducing flame gives the characteristic tungsten-blue bead.

Scheelite (Syn. Scheelspat) $CaWO_4$. It is next in importance to wolframite. It is white to yellowish, at times reddish to greenish in color, with an adamantine to vitreous lustre; density between 5.6 and 6; crystallizes in pyramids of the tetragonal system, sometimes of considerable size, but is also found in reniform and granular masses; its hardness is between 4.5 and 5 (about the hardness of apatite); it is brittle; its fracture is uneven; streak white; it is frequently accompanied by tin and copper minerals.

Scheelite is attacked by hydrochloric acid, leaving a yellow powder soluble in ammonia; fusible before the blow-pipe to a semi-transparent glass, with borax gives a transparent bead which becomes opaque on cooling; with salt of phosphorus a characteristic tungsten reaction if free from iron; varieties rich in iron have to be treated with tin on charcoal to show the tungsten coloration.

Wolframite $(Fe,Mn)WO_4$. It corresponds most frequently to the formula $Fe_3MnW_4O_{16}$. The mineral is opaque, color between dark brown and pure black, streak reddish brown. Density between 7.12 and 7.36, hardness between 5 and 5.5. It crystallizes in oblique rhombic prisms of the monoclinic system. Michel produced crystallized wolframite artificially by fusing in a crucible sodium tungstate with the chlorides of iron and manganese. The natural mineral has good cleavage and is usually associated with quartz, native bismuth, cassiterite and pyrite.

The ratio of FeO to MnO varies from 1 to 7 to 7 to 1. It is decomposed by aqua regia, leaving a residue of yellow tungstic acid; concentrated sulphuric and also hydrochloric acids attack it sufficiently to give a colorless solution, which turns blue on the addition of metallic zinc. It melts easily before the blow-pipe to a magnetic globule having a crystalline appearance. With salt of phosphorus in the reducing flame a dark red. Fused with carbonate of soda gives the characteristic manganese reaction.

Hubnerite $MnWO_4$. This mineral contains 76.4 percent. WO_3 and 23.6 per cent. MnO when pure. It occurs in foliated cleavable masses, reddish brown in color, has a high luster on the cleavage and is usually accompanied by fluorspar and apatite. Its density is 7.14, hardness 4.5, streak brownish yellow. It is soluble in hydrochloric acid, leaving a yellow residue soluble in ammonia.

It is less fusible before the blow-pipe than wolframite. With the fluxes reacts for tungsten and manganese.

Stolzite, $PbWO_4$. Has a grayish to greenish color, luster resinous to adamantine, density 7.9 to 8.1. It is isomorphous with scheelite, crystallizing in small, square pyramids usually in irregular groups. Its hardness is 2.75 to 3, streak uncolored.

It is decomposed by nitric acid, leaving a yellow residue of tungstic acid. Fuses easily before the blow-pipe to a crystalline bead. On charcoal with soda yields lead. With the beads the tungsten coloration.

Cuproscheelite, $CuCa_2W_3O_{12}$. Contains about 7 per cent. copper. It is a rare mineral found in small pistachio green crystalline grains.

The tungsten minerals always contain a small amount of molybdic, columbic, tantalic and phosphoric acids.

Tungsten occurs also in a large number of other minerals; particularly those which contain uranium, vanadium, niobium, tantalum, such as microlite, samarskite, yttrotantalite, niobite, etc. It is frequently associated with tin and also with titanium; a large part of the tungsten used in commerce comes from the treatment of the accessory tin minerals of Cornwall. At Malacca in Siam and in Upper Tonkin the cassiterite mined contains up to 30 percent. of wolframite. Certain zinc minerals also contain tungsten, and the by-products of the treatment of these ores are utilized in some English works for the production of tungstic acid.

DISTRIBUTION OF TUNGSTEN.

Wolframite.—There are a large number of known deposits, but very few actual mines. We may mention:

France: Chanteloube near Limoges, Mondelisse and Nepoulas, St. Leonard and Limousin, Vaulry (Haute-Vienne), Framont (Vosges), Meymac (Correze).

England: Ruro, St. Austell, Tavistock, East-Pole, Drakewalls (Cornwall).

Saxony: Altenberg, Graupen, Seyer, Zinnwald.

Bohemia: Schlangenwald, Ehrenfriedensdorf.

Spain and Portugal: Deposits of wolframite are found in the western part of the Spanish Peninsula in the northern, central and

eastern sections in Cambrian and Silurian granites and schists which have been strongly metamorphosed. The deposits in Portugal appear to be the richer. In general, they are characterized by a series of veins with a dominant direction of NW to SE. There are frequent cross veins and lenses workable by stoping. The analogy with the tin deposits is very close; veins are found containing either cassiterite or wolframite with either one or the other predominating.

Wolframite constitutes primarily a serious impurity in many tin ores; at present we may say the opposite from the intrinsic value of the two metals. The modern processes of treating mixed minerals either by electromagnetic means or chemical methods allow of the easy separation of the two minerals. However, the plants for the separation are expensive. The richer veins occur at the contact of the schists and granites; in general they are very irregular with numerous enlargements and stringers. The mineralization is variable and in general rather scanty except at the bottom of the pockets. The working is difficult and the relatively small amount of wolframite in the veins makes its extraction costly and scarcely sufficient for the increasing needs of metallurgy. The quartzose veins contain wolframite in the form of crystals more or less separated and broken, at times forming little veins of compact mineral a few centimeters in thickness and of limited extent.

The impurities are cassiterite, pyrite, arsenopyrite and chalcopyrite. Cassiterite can be separated by electro-magnetic treatment, and the other foreign bodies by mechanical treatment, which is relatively easy because of the great difference in density. In general, the rich ore is separated by hand picking, and crushers break up the rest to free the wolframite from the gangue in order to perform the commercial concentration. The most favorable concentration is to a product with 68 to 72 percent. of tungstic acid.

In Portugal wolframite is found in the following districts: Castello-Branco, Guarda, Vizem, Porto, Braganca, Rivaes and Villa-Real. The principal mines are:

Braga (Rivaes).
Aguas Ferrens and Mina Rebordosa (Porto).
Borralhas (Villa-Real).

Alvarengo (Areiro).
Panasqueira and Cabeco de Plao (District of Castello Branco).
Laborim (Villa Nova de Velha).
Carvalhal de Estanlo e Bodiosa (Vizen).
S. Margarida (Proenca a Velha).
Quarta-Feira (Sabugal).
Pinhel (Guarda).
Serra das Pedras de Valle das Mocas (Villa Nova da Paira).
Fonte da Batalha, Valle de Milho (Braganea).

America.—In America the production of wolframite in the United States from 1902 to 1909 was as follows:

1902, 184 short tons.
1903, 292 " "
1904, 740 " "
1905, 834 " "
1906, 928 " "

The ores are found in California, Washington, Idaho, South Dakota, Utah, Arizona and Colorado. At Saint Paul, Minnesota, the "Germania Mining Co.," recently formed of German capitalists, exploits a deposit of wolframite at Camp Germania, near Deertrail, Stevens County, Washington. In Colorado, Boulder County, tungsten is found in large quantities. Of the 834 tons produced in the United States in the year 1904, 600 to 700 tons came from Colorado. The principal deposits are at Salina, Wallstreet, Eldora, Gorden Gulch, Caribou and Nederland; the three last are the only ones at present worked. The principal companies in the field are the Boulder County Company, of Boulder, and the Colorado Tungsten Company, of Pittsburgh. The Boulder County mine has two veins striking N and S with a dip towards the east of 85°. The veins are 8 feet wide, and there is a shaft 145 feet in depth with two cross-cuts 30 and 40 feet. The Colorado Tungsten Company owns in Boulder County 730 acres of ground, 590 acres of which are situated close to Nederland, where the principal tungsten deposits are found. The deposit is 8 miles long, the southern end passing into Gilpin County, where the gold industry is of considerable importance. The sub-formation around Nederland is formed of schists and granites transversed by large andesite dykes. The ore is a breccia composed of wolframite and feldspar, the latter sometimes replaced by quartz.

The ore goes through a simple mechanical preparation; crushing, grinding in brocarbs and then in tube mills, classification in spitzkasten and on Wilfley tables. The extraction is 70 to 80 percent. of the tungsten contents of the ore, and the concentrates contain 60 to 70 percent. of tungstic acid. Most of the concentrating mills are independent of the mines. Some treat the ore at a certain charge per ton, others buy the ore, paying for 3 percent. less than its actual tungsten content. The mines which have their own concentrating mills can treat ore containing 2 percent. tungstic acid. The ore contains very little phosphoric acid. The production of this district amounted in 1905 to 720 tons of tungstic acid, and in 1906 to 820 tons; at the present time it is 100 tons a month.

In Utah, up to the present, tungsten has been found in only small quantities and constitutes a secondary product of the Continental Alta mine at Little Cottonwood.

In Arizona, hubnerite has been found about two miles west of Johnson, Cochise County, in deposits of sand and in small quantities in quartz veins. The mineral is separated by air concentration in a sort of jig. The deposits are known to extend for several miles. The work is mostly done by Mexican miners, who receive 10 cents per pound of concentrate. One workman will handle up to 20 tons of ore per day. The grains of concentrate are from 0.1 inch to 1 inch in size and consist of 65 to 70 percent. of wolframite and the rest scheelite. They sell on the spot at 17 to 20 cents a pound. The production of the district is 4 to 5 tons a month. The quartz veins found in Arizona and known to contain wolframite have not been exploited because the sand deposits are very easy to work. A hand hammer does the breaking and the labor charges are not high. Thus there is very little fixed cost for installation of ore dressing plant. It should, however, be remarked that the proposition is being handled in a very imperfect manner, and the waste from this method of working is at times very high.

Australia: Sluisbox Camp.

Tonkin: Nam Kep and Beau Site, both producing a tungstiferous cassiterite.

DISTRIBUTION OF SCHEELITE.

France: Framont (Vosges) and Meymac (Correze).

Cornwall: East Pole.

Saxony: Marienberg, Altenberg, Bipsberg.

Bohemia: Schaggenwald, Ehrensfriedensdorf.

New Zealand: Waipori, Lake Vatakipu.

Sweden: Bitzberg.

Finally, there are deposits of scheelite and wolframite in Norway, in the Tyrol, in Piedmont, in Bolivia, and in Canada.

Analyses of Tungsten Ores.

I. Wolframite.

	Tungsten Company		Campredon			Carnot	Gin	Gin (Hubnerite)
Tungstic Acid .	71.50	71.78	74.60	73.—	63.75	74.75	65.16	71.95
Columbic Acid .	. .	. .	. .	. .	. .	. . .	. . .	. . .
Tantalic Acid . .	. .	. .	. .	. .	. .	0 95	1.26	. . .
Oxide of Iron .	8.18	14.94	12.81	12.18	16.—	16.17	15.22	1.20
Oxide of Mangan.	17 77	10.86	11.12	11.58	8.90	6.40	4.89	21.98
Silica	2.40	0.60	0.70	1.20	8.62	1.12	9.64	2.27
Cassiterite . . .	. .	. .	. .	. .	. .	. . .	0.40	. . .
Alumina	. .	. .	0.21	. .	1.83	. . .	. . .	0.20
Phosphoric Acid	. .	. .	. .	. .	. .	. . .	0.20	. . .
Copper Oxide .	. .	. .	0.01	0.10	0 03	. . .	0 84	. . .
Arsenic	. .	. .	. .	. .	0.06	. . .	0.08	. . .
Lime	. .	. .	. .	. .	. .	0.40	0.08	. . .
Combined Water	. .	. .	. .	1.65	. .	. . .	} 2.03	. . .
Not determined .	. .	. .	. .	0.29	. .	. . .		2.40

II. Scheelite.

	Monroe	Meymac	Chili	Tyrol	Canada
	Bowen	Carnot	Gin	Gin	Gin
Tungstic Acid . .	76.05	74.50	78.02	75.40	69.50
Lime	19.36	18.70	17.06	18.60	16 04
Oxide of Iron . .	1.03	1.05	2.18	1.25	0.54
Oxide of Mangan.	0.31	0.30	0.74	0.77	0.18
Phosphoric Acid .	. . .	. . .	0.20	0.18	0.14
Silica	2.54	5.20	2.70	2.90	12.46

CONSUMPTION OF TUNGSTEN MINERALS.

The total consumption of tungsten minerals may be estimated at 3,600 tons of 60 to 70 percent. concentrates which would represent 20 to 25,000 tons of crude ore.

The ore is generally sold with a guarantee of more than 50 % tungstic acid, a maximum content of 0.2 % phosphorus, 0.01 % sulphur and 1 % of cassiterite.

The price of the ore is very variable, for the demand often exceeds the supply and many of the sources of supply are irregular. In the last four years the price has varied between the following limits:

70 to 75 %	WO_3,	$5.60 to $9.00	per	unit	per	ton.
65 to 70 %	"	$5.40 to $8.60	"	"	"	"
60 to 65 %	"	$5.00 to $8.00	"	"	"	"

The principal market of tungsten ores is at Hamburg, where the annual sale amounts to over 1,500 tons.

INDUSTRIAL CHEMISTRY OF THE COMPOUNDS OF TUNGSTEN.

MECHANICAL PREPARATION OF TUNGSTEN ORES.

The classification and mechanical concentration of tungsten ores is relatively simple because of the high gravity of all tungsten compounds. Nevertheless the hydro-mechanical processes are insufficient to insure complete separation of cassiterite, in this case it being necessary to resort to magnetic separators.[1]

It is not superfluous to recall here the principles of the magnetic separator. If magnetic or non-magnetic particles are introduced into a non-homogeneous magnetic field, the former tend to go towards the portion of the field of maximum intensity. Apparatus working on this principle are called direct extraction machines and deviation machines. In the direct extraction apparatus the magnetic attraction raises the magnetic particles and carries them to a suitable receiver. In the deviation apparatus the trajectory of a freely falling body is affected by magnetic attraction.

There are a great number of forms of apparatus used on tungsten ores, such as the separators of Mechernich, Johnson, Wetheril, Rowand, Knowles, King, etc.

Korda gives the following results:

[1]See désiré Korda: The Electromagnetic Separation of Minerals.

1. Experiments in the Laboratory of Mechernich, made by Langguth on a mixed tin-tungsten ore from Australia.

		Per cent. Sn.	Per cent. W.
	Original ore	33.3	14.2
Separated	Tin ore	61.5	Trace
	Tungsten ore	Trace	42.4

2. With a Wetheril apparatus, 9,690 kilograms of Spanish tin and tungsten ore containing 48.5 % tin and 22.5 % tungstic acid was treated, being first freed from iron by a preliminary magnetic treatment. This product was then passed through the Wetheril apparatus excited with a current of 10 amperes at 50 volts, and then a second apparatus using 6 amperes at 30 volts. The products were:

30.7 % wolframite containing 73.2 % WO_3 and 0.8 % Sn; and 68.5 % cassiterite containing 70.5 % Sn and 1.1 % WO_3.

The Nam-Kep (Tonkin) company had some of this ore treated by the Humboldt company at Kalk, near Cologne, with practically identical results. Unfortunately, the magnetic separation is not so well adapted to all ores and with some of them the results are absolutely discouraging.

In Portugal, the ores are treated as follows: The run of mine is first hand picked and then broken in jaw crushers, treating 10 tons per hour, to a maximum sized product of 4 cm. This is then put through ball mills which reduce it to 40 mesh per square centimeter. The powder is then washed, the hydraulic concentrates running 60 to 65 % and even 70 % WO_3. Magnetic separation has not been employed up to the present.

PURIFICATION OF TUNGSTEN ORES AND MANUFACTURE OF TUNGSTIC ACID.

The chemical treatment of the mechanical concentrates and the production of tungstic acid are based on the following principles:

1. The alkaline carbonates attack in the dry way insoluble tungstates and form soluble alkaline tungstates.

2. Mineral acids precipitate tungstic acid from tungstates in solution in a form insoluble in the solution.

3. Ammonium tungstate is decomposed at redness in an oxidizing atmosphere into tungstic acid.

4. Tungstic acid and tungstates are attacked by hydrochloric acid gas forming the oxy-tetra-chloride of tungsten, easily volatile, and decomposed by water into tungstic acid and hydrochloric acid.

5. Solutions of alkaline tungstates are transformed into sulpho salts by the action of hydrogen sulphide. On decomposing the sulpho-tungstate by a dilute acid the only slightly soluble tungsten trisulphide is formed.

TREATMENT OF WOLFRAMITE.

Attack by aqua regia.—This is a laboratory process consisting in dissolving the finely powdered mineral in hot aqua regia containing an excess of hydrochloric acid. After evaporating to dryness on a hot-air bath and washing to eliminate iron and manganese salts, the residue is treated with ammonia to dissolve tungstic acid. On concentrating, the liquor deposits crystals of ammonium tungstate, from which the tungstic acid is obtained by calcination. This method of procedure does not separate tungsten from tin nor does it eliminate columbic or tantalic acids. It is true that the last two are only present in small quantities, so small as to present no inconvenience to subsequent metallurgical operations.

To separate tungstic acid from columbic and tantalic acids, one can digest the impure material with ammonium sulphide, which dissolves tungstic acid, but not the others.

Attack by alkaline carbonates.—This process is the one generally used in the tungsten industry. The wolframite, finely pulverized, is fused with sodium carbonate with the addition of nitrate. The fusion is done in a reverberatory furnace on a hearth of dolomite agglomerated with tar and burned in place. After the fusion, the mass is broken up, granulated, digested with water in filter tanks with methodic washing, using nearly boiling water. The alkaline tungstate dissolves, at the same time silica and phosphoric acid also dissolve as silico-tungstate and phospho-tungstate of sodium. The metallic oxides remain insoluble.

In the presence of alkaline nitrate manganese will form a little soluble manganate which likewise dissolves, but the presence of this body is not objectionable in most cases. If necessary, it can

be separated after the silica and phosphoric acid have been eliminated. To eliminate these two latter impurities hydrochloric acid is added to the boiling solution to acid reaction, the neutral tungstate passes to the form of para-tungstate, $5Na_2O.12WO_3$, soluble in hot solution, but precipitated cold in fine prismatic crystals. The silico-tungstate and phospho-tungstate of sodium are more soluble and remain in the mother liquor.

The para-tungstate, after being filtered out, is washed and transformed back again to the normal tungstate by the addition of caustic soda. Tungstic acid is then obtained from this solution by the addition to it when boiling of hydrochloric acid. Care should be taken to pour the tungstate into the acid and not the acid into the tungstate, for in the latter case there will be formed at once tungstic acid, which will, however, combine with the neutral tungstate to form the para-tungstate which is very difficult to decompose.

To recover the tungstic acid remaining in solution with the silica and phosphoric acid the solution is precipitated by carbonate of lime and treating the precipitate formed by one of the methods given for treating scheelite.

The above-described processes are in general use, although they are really onerous, because of the large quantities of reagents necessary and also because there are considerable losses on account of the slight solubility of the precipitates.

Berzelius modification of the alkaline method.—Berzelius modified the preceding process by passing into the solution of alkaline tungstate obtained as above a current of hydrogen sulphide gas, obtaining thus in solution the sulpho-tungstate:

$$K_2WO_4 + 4\ H_2S = K_2WS_4 + 4\ H_2O$$

The action of the hydrogen sulphide should be prolonged, for, if not sufficient, the monosulpho-tungstate K_2WO_3S and the trisulpho-tungstate K_2WOS_3 may be formed:

$$K_2WO_4 + H_2S = K_2WO_3S + H_2O$$
$$K_2WO_4 + 3\ H_2S = K_2WOS_3 + 3\ H_2O.$$

When the reaction is complete the solution has a fine reddish orange color, then excess of hydrochloric acid is added, which causes the precipitation of tungsten trisulphide:

$$K_2WS + 2\ HCl = WS_3 + 2\ KCl + H_2S.$$

The hydrogen sulphide disengaged in this reaction may be utilized for the decomposition of a fresh quantity of alkaline tungstate, but only one-quarter of the hydrogen sulphide originally used can be thus regained. It is necessary to operate always with excess of acid present and in cold solution, for the tungsten trisulphide is slightly soluble in pure water and still more so in boiling water, but is insoluble in cold solution in the presence of acid. The precipitation is somewhat difficult and is complete only on boiling in the presence of considerable hydrochloric acid. In cold dilute solution a dark brown solution of colloidal sulphide is obtained. The sulphide is filtered out, washed with water acidulated with nitric acid, dried, and roasted in the presence of air at a low red heat.

Process of F. Jean.—The wolframite, ground to a very fine powder, is mixed with 3 per cent. of calcium carbonate and 20 to 30 per cent. of sodium chloride, and heated for a half hour in a crucible in a reverbatory furnace. The reaction is as follows:

$$Fe_3MnW_4O_{16} + 8\ NaCl = Na_2WO_4 + 3\ FeCl_2 + MnCl_2.$$

When the mixture has cooled it is pulverized, boiled with hydrochloric acid to dissolve the lime and the oxides of iron and manganese, disengaging chlorine, and leaving all the tungstic oxide as an insoluble lemon-yellow powder. The process is applicable only to very pure wolframite, for it does not eliminate silica, which is not attacked but very little by sodium chloride.

Process of Gin.—The author heats in a reverberatory furnace with an agglomerated dolomite hearth at a temperature of 1,200 to 1,300° C., a mixture of finely pulverized wolframite with magnesium chloride. There is formed magnesium tungstate and a certain proportion of chlorides of iron and manganese which almost entirely distil off. On continuing to heat with an oxidizing flame the iron remains as a peroxide. The mass is cooled, pulverized, treated with a small quantity of cold water to dissolve the chlorides and to leave undissolved the crystals of magnesium tungstate. The residue is then taken up in boiling water, the oxides of iron and manganese remain insoluble, likewise silica. The tungstic acid is in solution as magnesium tungstate which crystallizes after concentration as vitreous tufted prisms of the formula $MgWO_4 . 7H_2O$.

Some silica will remain in solution as silico-tungstate. The mother liquor is decanted, wash water added to it, and it is then treated with ammonium carbonate to precipitate the magnesia and keep the tungstic acid in solution. On evaporating ammonium tungstate is obtained, which is decomposed by calcination.

If the amount of silica remaining in solution is large the purification may be terminated by the use of bi-sulphate of potassium, as will be described further on, but this supplementary attack is never necessary when the tungstic acid is to be used for the manufacture of metallurgical products.

Attack by bi-sulphates: Modification of Gin.—Attack by bi-sulphates has been used industrially for a long time, but it presents certain difficulties which need radical modification. Good results are to be obtained by proceeding as follows: The ore is decomposed in a muffle furnace, the hearth of which is made of silica agglomerated with pitch, well stamped in place and then calcined before being used. The bi-sulphate is then fused with the orifices of the muffle closed. When the fusion is complete the door is opened and the finely pulverized wolframite is thrown in. The mass is continually stirred and the temperature raised until the whole is fluid enough to run out. The mass, after solidification, is broken up, finely pulverized and treated with water, which dissolves soluble sulphates of the metals and phosphoric acid and leaves insoluble potassium acid tungstate as a white amorphous mass. This insolubility of the acid tungstate is true only of acid solutions which necessitates the use of an excess of bi-sulphate above that indicated by the following reaction.

$$5\,Fe_3MnW_4O_{10} + 24\,KHSO_4 + 4\,H_2O =$$
$$\underbrace{4(2\,K_2O.\,5\,WO_3.\,4\,H_2O)}_{\text{Insoluble.}} + \underbrace{15FeSO_4 + 5MnSO_4 + 4K_2SO_4}_{\text{Soluble.}}.$$

In practice, about 50 % excess of bi-sulphate is used so as to insure complete attack, supply loss, and keep in the solution sufficient acid to insure the insolubility of the tungstate, while at the same time it insures the solution of any phosphates which may be present.

The insoluble residue after separation from the acid solution consists not only of tungstic acid, but also of silica, cassiterite and

insoluble sulphates. It is dried and treated with warm water at 40°, containing some ammonium carbonate, or cold water may be used, to which is added ammonia and a current of carbonic acid passed through. Under these conditions, the acid tungstate dissolves, while the silica and cassiterite remain insoluble:

$$(2K_2O.5WO_3.4H_2O + 5(NH_4)_2CO_3 = 2K_2CO_3 + 5(NH_4)_2WO_4 + 3\,CO_2 + 4\,H_2O.$$

In reality, the neutral ammonium tungstate is not obtained, but on evaporation of the solution paratungstate is produced, while the ammonia in excess escapes until a salt of the following composition results: $5(NH_4)_2O.12WO_3 + nH_2O$, in which n varies from 11 to 5 according to the temperature of evaporation. The salt obtained crystallizes in plates or in acicular forms; it loses water of crystalization at 100°; when heated in contact with the air it is decomposed, leaving tungstic acid containing a little nitrogen which causes no inconvenience in metallurgical work, for the nitride and the oxy-nitride are both decomposed above 1,200° C.

If a purer tungstic acid is required, as for chemical uses, the ammoniacal solution is treated with hydrogen sulphide to form ammonio-sulpho-tungstate. This salt, only slightly soluble in cold water, deposits in the form of orange red orthorhombic crystals. On heating these crystals the trisulphide results, which may be roasted to tungstic acid. The sulpho-tungstate remaining in solution may be obtained by treating with hydrochloric acid in excess which precipitates pure trisulphide. In both the methods above described there is considerable loss of ammonia. This may be regained by treating the solution of paratungstate with lime and boiling and catching the ammonia which is disengaged, while the calcium tungstate precipitated may be utilized directly in some metallurgical operations.

Bi-sulphate process of the Kempen Electrochemical Factory.—This company heats sodium bi-sulphate with mono-hydrated sulphuric acid, and when fusion has commenced the finely pulverized mineral is introduced, enough bi-sulphate being present to transform all the tungsten into sodium acid tungstate; the decomposition is rapid.

The solution obtained by washing contains the tungsten as sodium acid tungstate and some of the foreign matter present as sulphates. The latter may be precipitated by electrolysis. The residual solution is evaporated, the sodium sulphate deposited is removed, and the tungstic acid precipitated by the addition of hydrochloric acid. This process was patented in Germany in 1902, No. 149,556, and differs only slightly from the previous one which I have personally devised.

TREATMENT OF TIN BEARING ORES.

Some tungsten ores contain notable quantities of cassiterite. It might be more exact to say that wolframite is often found in large proportion in tin ores, such as those of Saxony, Bohemia, Cornwall, Australia, Portugal and Upper Tonkin.

Under these conditions, the complete separation of cassiterite is necessary and should be effected so as to utilize the tin mineral for the tin content. Although attempts at magnetic separation have shown very favorable results, it appears doubtful, however, if it is satisfactory in all cases.

I have studied the treatment of tin minerals from Upper Tonkin, Beau Site deposit, which were recently imported into Europe. This alluvial ore, formed of the disintegration of veins, furnishes 3 to 8 kilograms of cassiterite-wolframite per cubic meter, which can be extracted by mechanical separation, giving a final product with 55 to 60 % cassiterite and 25 to 30 % wolframite. It was first tried to separate these two minerals by electro-magnetic means, which resulted, however, in three concentrates, increasingly rich in cassiterite and decreasingly rich in wolframite, but with no sharp separation. Finally a separation was made in a German works, which gave a wolframite concentrate containing not more than 1 % tin. However, since the presence of cassiterite even in small proportion is always very deleterious to wolframite because of the brittleness which tin imparts to steels, it will be certainly more advantageous to treat directly the mixed concentrate by the bi-sulphate method, omitting entirely the magnetic separation. It is only economical to treat by the chemical method concentrates rich in tungsten.

EXAMPLE OF THE TREATMENT OF CASSITERITE-WOLFRAMITE.

Assume a hypothetical mixture containing:

WO_3	27.80 %
FeO	5.00 %
MnO	3.66 %
SnO_2	57.00 %
SiO_2	0.60 %
CaO,MgO	5.60 %
Undetermined	0.34 %

This composition corresponds, per ton, to the formula, $(1.2\ WO_3.0.7\ FeO.\ 0.5\ MnO) + 3.8\ SnO_2 + 0.1\ SiO_2 + Ca\ O)$. Attacking the mineral, as represented by the ton formula just given, with five molecules of bi-sulphate there is obtained, allowing for loss of SO_3:

Insoluble, $3.8SnO_2 + 0.24\ (2K_2O.\ 5\ WO_3.\ 4H_2O) + 0.1\ SiO_2 + CaSO_4$.

Soluble, $0.7\ FeSO_4 + 0.5\ MnSO_4 + 1.2\ K_2SO_4 + 1.56\ KHSO_4$.

Treating the insoluble material further by 2 molecules of ammonium carbonate, the tungstic acid is made soluble, as has been explained, and the final loss is only one-quarter of a molecular weight. The residue remaining will have the formula: $3.8\ SnO_2 + 0.1\ SIO_2 + CaSO_4$. That is to say, the residue is a tin ore containing 80 % cassiterite or 63 % tin, and may be enriched to 75 % tin by prolonged washing to remove the calcium sulphate. The cost of the operation is not an obstacle since only the reagents to separate the tungsten are used. On the other hand, the soluble sulphates may be regenerated since the potassium is found therein in its entirety.

Supposing that the tin ore is worth $7.00 per unit of cassiterite based on 70 % content with a reduction of $0.07 for each unit below 70 %, and assuming that the tungsten ore is worth $8.00 a unit for a 70 % ore with a reduction of $0.08 for each unit below 70 %, so under these conditions the cost of a ton of ore would be:

$$57\ [7 - 0.07\ (70 - 57)] + 27.8\ [8 - 0.08\ (70 - 27.8)] = \$420.$$

If we consider $440 to cover everything, we may figure out as follows the cost of the operation and the products:

Cost of Treatment of a Ton of Cassiterite-Wolframite.

One ton of ore 57 percent. SnO_2 and 27.8 percent. WO_3	$440 00
Bi-sulphate of potassium, 680 kg. @ $40 per ton	27 20
Ammonium carbonate, 200 kg @ $160 per ton	32 00
Coal for the fusion and the evaporation, 1 ton @ $5.00	5 00
Labor	3 60
Handling of materials	2 00
Depreciation of equipment	4 00
Interest on ore in stock and in treatment	2 20
General expenses and unforseen	4 00
Total	$520 00

Products Obtained.

Tin ore, 75 percent. tin, 575 kg @ $520 per ton		$299 00
Tungstic acid, 200 kg @ $900 per ton	$234 00	
Premium on excess purity, $0.04 per kg	10 40	
		244 40
Ammonia, 22 percent. NH_3, 100 kg @ $6.40 per 100		6 40
Potassium sulphate		10 20
Total		$560 00

The operation would therefore be profitable for the commercial purchase of the ore and would be more so for the producer himself.

PREPARATION OF TUNGSTIC ACID FROM SCHEELITE.

Decomposition by acid.—Pure scheelite is treated with concentrated hydrochloric acid or nitric acid, forming chloride or nitrate of calcium in solution, and an insoluble residue containing the tungstic acid. Washing and calcining the residue gives a crude tungstic anhydride.

If the scheelite is impure, especially if silicious, the operation must be modified slightly; the ore is attacked by dilute nitric acid, generally hot, or by concentrated hydrochloric acid. The lime being dissolved with the metallic oxides, the residue is washed and treated with ammonia to which ammonium carbonate is added. Ammonium tungstate goes into solution and may be crystallized out, while the lime is precipitated as carbonate along with the silicious residue. Tungstic acid is obtained from the ammonium tungstate by calcination.

Fusion with alkaline fluoride.—Scheelite is fused with potassium

fluoride in a reverberatory furnace, producing soluble alkaline tungstate and insoluble calcium fluoride, easily separated. The solution of alkaline tungstate is decomposed by hydrochloric acid, taking precautions, if necessary, to eliminate impurities from the precipitate.

GIN'S METHOD FOR THE PREPARATION OF TUNGSTIC ACID BY MEANS OF TUNGSTEN OXY-TETRA-CHLORIDE.

The residue of impure tungstic acid obtained by means of the processes previously described may be used for the preparation of pure tungstic acid by converting the same into a volatile tungsten compound which can be separated from the other impurities.

The crude material is dried and mixed with a mixture of ferric sulphate and sodium chloride, on heating for a short time below 400°, the following reactions take place:

$$3\ Fe_2(SO_4)_3 + 6\ NaCl = 3\ Na_2SO_4 + 2\ FeCl_3.$$
$$3\ WO_3 + 4\ FeCl_3 = 3\ WOCl_4 + 2\ Fe_2O_3.$$

The oxy-tetra-chloride $WOCl_4$ melts at 210° and boils at 227° C. It crystallizes in magnificent ruby-red needles, transparent, and easy to catch in a metallic condenser. When thrown into water it decomposes almost immediately into tungstic acid and hydrochloric acid:

$$WOCl_4 + 2\ H_2O = WO_3 + 4\ HCl.$$

The only impurity to be feared may be a little ferric chloride carried into the condenser and which is partially decomposed by water to form Fe_2O_3. This contamination is very small, and if it occurs accidentally the condensed product may be redistilled at 230°, volatilizing the $WOCl_4$, which boils at 227° and leaving the $FeCl_3$, which boils at 280°. Further, if the vapors are condensed in cold water the decomposition of the ferric chloride is so slight that the precipitate of WO_3 after washing is practically pure. This decomposition of ferric chloride is increased as the liquor becomes more acid from the decomposition of the $WOCl_4$.

GENERAL OBSERVATIONS.

The processes which have been described and which are relatively simple in their application may be used for other tungsten minerals than wolframite and scheelite. Sometimes they are

inapplicable and some ores of tungsten are so rich as to be used without these treatments. One may say in general here that it is necessary for the development of the electrometallurgy of tungsten to manufacture the metal and its alloys only from pure, raw material or purified compounds.

The manufacturers of ferro-tungsten have, up to the present, frequently reduced wolframite concentrates directly in the electric furnace, and, excepting where they have used very pure ore, they have naturally obtained ferro-tungsten containing a large proportion of manganese, carbon and sometimes phosphorus. Such impurities cause inconvenience and are very prejudicial to the use of tungsten in the metallurgy of steel. For this reason many users of tungsten prefer to use the tungsten powder obtained by reduction of tungsten acid by means of zinc, in spite of the greater difficulty of using the metal in this form.

Allowable Impurities in Tungsten Alloys.

The metallurgy of steel does not rigorously require tungsten free from carbon, and the carbide with 3 per cent. of carbon may generally be employed directly in perlitic steels with a somewhat moderate content of tungsten. For special steels for tool purposes, containing in general more than 10 per cent. tungsten the carbon content is of much greater importance, but may be solved by the choice of a very soft steel, so soft as to keep the final content of carbon under the requirements.

However, it is a remarkable fact that the introduction of tungsten in the form of carbide gives different properties to a metal of similar composition. It seems that to obtain uniform results tungsten must be added in the pure form or in the form of ferro-tungsten. Carbon must be absent in the alloys of copper and tungsten and aluminium and tungsten, alloys which are increasing in commercial application. Pure tungsten is required in the production of platinoid, an alloy of the composition Cu 60 per cent., Zn 25 per cent., Ni 14 per cent., W 4 per cent. The tungsten used in the manufacture of partinium must also be free from carbon.

Tungsten to be used in steel manufacture must not contain more than 0.05 per cent. P, since a higher content would be decidedly harmful to high speed steels containing 12 to 15 per cent. of tungsten.

The maximum allowable limit of sulphur is 0.1 per cent. For high speed steels more than 0.50 per cent. Mn, and 0.20 per cent. Si is not permitted; that is to say tungsten intended for the manufacture of high speed steel must be made from pure tungstic acid or from ferro-tungsten obtained from non-manganiferous wolframite.

MANUFACTURE OF CAST TUNGSTEN.

ELECTROTHERMIC METHOD.

Cast tungsten not high in carbon may be produced by direct treatment in the electric furnace of a mixture of tungstic acid and carbon, using a little less carbon than is indicated by the reaction:

$$WO_3 + 3\ CO = W + 3\ CO.$$

If the mixture is treated in a furnace having electrodes and two contiguous hearths, using as the intermediate electrode a trough filled with tungsten, carburized or not, there is produced in the fused slag an upper reduction zone and a lower oxidation zone at the contact of the slag and the metal. It is in a certain sense automatic refining. In this manner tungsten may be obtained containing less than 2 per cent. carbon.

On adding to the metal made in the furnace 20 per cent. of its weight of soft iron cut into pieces of convenient length the carbon content may be reduced to 1.5 per cent. and this carbon content may be reduced still lower by putting a bath of melted tungsten dioxide on the surface and keeping carbon away.

The energy density most convenient to use is 130 to 140 watts per square centimeter section of electrodes, with a voltage of 50 to 60 volts for the two hearths.

When pure tungsten anhydride is used as a fused slag, some is lost by volatilization, which loss may be avoided by using a slag formed of tungstic anhydride and magnesium aluminate to which fresh tungstic anhydride is added as the operation proceeds.

If the tungstic anhydride or the tungsten dioxide is only at hand as powder the CO gas formed as it escapes may cause considerable loss. This may be avoided by mixing the anhydride or the dioxide with carbon and agglomerating it with 4 to 5 per cent. tar and 2 to 3 per cent. dry bran. The mass is mixed hot in a mechanical mixer or rabbled by hand and pressed into oval

bricks. This may be used in the furnace without hindering the escape of CO and without causing loss by dusting. If a briquetting machine is not at hand the mixture may be stamped by hand and broken up by a hammer when cold.

If it is desired to manufacture a cast tungsten with more carbon in it it is only necessary to add more than the proportions stated above.

REDUCTION BY CALCIUM CARBIDE.

By heating tungstic acid or dioxide with calcium carbide in the presence of silica tungsten carbide and calcium silicate are formed:

$$6\ WO_3 + 7\ SiO_2 + 7\ CaC_2 = 7\ CaSiO_3 + 3\ W_2C + 11\ CO.$$
$$6\ WO_2 + 5\ SiO_2 + 5\ CaC_2 = 5\ CaSiO_3 + 3\ W_2C + 7\ CO.$$

These reactions have not been used industrially for the reason that the tungsten carbide will contain all the sulphur and the phosphorus that were originally present in the calcium carbide. The author has tested this method by simply throwing tungsten dioxide into a calcium carbide furnace when running. The reaction goes on rapidly, and after two hours and a half of reduction in a furnace in full operation using 300 kilowatts, there was run out 154 kilograms of tungsten containing 3.1 carbon.

PRODUCTION OF FERRO-TUNGSTEN WITH LOW CARBON CONTENT.

The refining of cast tungsten to diminish its carbon content can be easily done in one of the furnaces which I have described for the treatment of molybdenum, especially in the Gin induction circulating furnace.[1]

The fused metal being introduced into the channels of this furnace, it is covered with hammer scale and a rapid reduction takes place according to the following formula:

$$Fe_6O_7 + 7\ W_2C = (6\ FeW_2 + W_2) + 7\ CO.$$

However, the reaction is not quantitative since there is always formed some ferrous tungstate by the following reaction:

$$Fe_6O_7 + 3\ W_2C = 5\ FeW + FeWO_4 + 3\ CO.$$

By these reactions it is possible to make ferro-tungsten containing over 80 per cent. tungsten and less than 0.5 per cent. carbon.

[1]See Transactions; Vol. XII, p. 441.

It is better not to try to make a tungsten alloy of higher tungsten content, for the richer alloys are not easily fusible and cannot be used for the manufacture of special steels by addition directly to the casting ladle.

The preceding reaction is never complete as far as the elimination of carbon goes, there always remaining at least 0.3 per cent., an amount which is of no consequence in the manufacture of steel.

Ferro-tungsten with less than 80 per cent. tungsten may be prepared very simply by adding metallic iron to the bath and decarburizing with oxide of iron or hammer scale:

$$3\ W_2C + Fe_2O_3 + n\ Fe = 3\ CO + 3\ FeW_2 + n\ Fe.$$

Decarburization by ferric oxide will yield alloys with as low as 0.15 per cent. carbon.

The electric furnace with flowing electrodes may likewise be used. The carburized tungsten is cast into electrodes which are used in the furnace with contiguous hearths, using as the intermediate electrode melted soft steel. Two arcs are drawn to the intermediate electrode and the bath is formed above it of tungstic dioxide and magnesium aluminate. The electrodes melt and their carbon is burned out by the WO_2. The resulting metal will contain not more than 0.15 to 0.25 per cent. carbon.

It should be noted always that the oxidation of the carbon by oxide of iron results in the formation of tungstate of iron; the amount thus formed may be reduced considerably by using silica, forming ferrous silicate according to the reaction:

$$W_2C + Fe_2O_3 + 2\ SiO_2 = W_2 + 2\ FeSiO_3 + CO.$$

THE SILICO-THERMIC PROCESS OF GIN.

This process, employed by Gin in 1898 and which has been reinvented several times since by other electrometallurgists, is based on the reaction of ferro-silicon on an alkaline earth tungstate at a high temperature.

In the electric furnace with two contiguous hearths in series the carbon electrodes are replaced by ferro-silcon electrodes, the intermediate electrode being likewise formed by a bath of ferro-silicon. Upon this a fluid bath of calcium tungstate is formed, the silicon oxidizes at the expense of the tungstic acid and combines with the lime to form slag while the iron unites with the tungsten.

With 20 per cent. ferro-silicon the reaction appears to take place as follows:

$$3\,CaWO_4 + 4\,Fe_2Si = (2\,Fe_2W + Fe_3W) + 3\,CaSiO_3 + FeSiO_3.$$

However, the slag which I obtained in my experiments always contained some tungsten and it is possible that the more minute study of the operation would show the formation of a silico-tungstic anhydride.

With 33 percent. ferro-silicon the reaction is:

$$3\,CaWO_4 + 4\,FeSi = 3\,FeW + 3\,CaSiO_3 + FeSiO_3.$$

With 50 per cent. ferro-silicon the reaction is:

$$3\,CaWO_4 + 2\,FeSi_2 = FeW_3 + 3\,CaSiO_3 + FeSiO_3.$$

These last two reactions are conjectured from observations made on the 20 per cent. ferro-silicon.

The process just described was tried with a furnace large enough to prove that it could be applied on a commercial scale. The reaction can easily be obtained in the circulating induction furnace containing a bath of ferro-silicon and throwing tungsten dioxide on its surface. It is necessary to use an energy density of 1,000 to 1,300 watts per cubic decimeter of metal contained in the channels of the induction furnace.

DATA ON THE COMMERCIAL MANUFACTURE OF FERRO-TUNGSTEN.

For fixing our ideas assume an ore represented by the following formula, expressed in kilogram molecules per ton of ore:

$$(1.5\,FeO.\ 1.5\,MnO.\ 3\,WO_3) + SiO_2,$$

corresponding to the percentage composition,

WO_3	69.60 %	W = 55.20 %
MnO	10.65 %	Mn = 8.25 %
FeO	10.80 %	Fe = 8.40 %
SiO_2	6.00 %	
Misc.	2.95 %	

The reaction of reduction may be written:

$$(1.5\,FeO.\ 1.5\,MnO.\ 3\,WO_3) + SiO_2 + CaO + 14.5\,C = (0.5\,Fe_3C.\ 0.5\,Mn_3C.\ 1.5\,W_2C) + CaSiO_3 + 12\,CO.$$

The weights of materials used and products obtained may be tabulated as follows:

1,000 kg ore.....(1.5 FeO. 1.5 MnO. 3 WO_3), SiO_2
174 kg carbon (220 kg coke) . 14.5 C
56 kg lime.....CaO
748 kg ferro-mangano-tungsten
of 73.8 per cent. W..... 1.5 W_2C, 0.5 Mn_3C, 0.5 Fe_3C
Slag .....$CaSiO_3$
Carbon monoxide .....12 CO.

Electric Energy Required for Reduction.

The following calculation is only approximately correct, for the heat of formation of W_2C is not known, nor the total heat in the fused alloy obtained. Using some figures from analogy, we can fill out the heat balance sheet as follows:

HEAT OF REACTION.

Initial State	$MnWO_4$ 1.50 × 338,000	507,000	Cal.
	$FeWO_4$ 1.50 × 331,000	496,500	"
	SiO_2	179,600	"
	CaO	145,000	"
	Total	1,328,000	"
Final State	W_2C 1.50 × 10,000 (?)	15,000	Cal.
	Mn_3C 0.50 × 9,900	4,950	"
	Fe_3C 0.50 × 6,600	3,300	"
	$CaSiO_3$	344,000	"
	CO 12 × 29,400	352,800	"
	Total	720,050	"
Heat balance of reaction		608,050	Cal.

SENSIBLE HEAT IN PRODUCTS.

Heat in fused alloy at 2,200° 748.5 kg × 660 =	494,010	Cal.
Heat in fused slag at 2,200° 116 kg × 640 =	74,240	"
Heat in carbon monoxide at 1,600° 12 (6.8 × 1,600 + 0.0006 × $1,600^2$) =	149,000	"
Total	717,250	"
Total heat requirement	1,325,300	"

Allowing for a loss of 6 per cent. of the materials charged, this corresponds to 1,900,000 calories per ton of alloy produced.

Assuming the thermal efficiency of the furnace to be 60 per cent., the above figure corresponds in round numbers to an expenditure of 3,700 kilowatt-hours per ton of alloy produced.

In industrial processes it is usual to assume a higher power consumption than the above calculated because the energy is applied usually in too small a space and causes the useless volatilization of part of the materials.

PRACTICAL FIGURES ON THE MANUFACTURE.

Consumption and production.	Per ton. Ore.	Alloy.
Ore: wolframite containing 70 percent. WO_3	1,000 kg	1,400 kg
Lime	60	84
Coke	220	300
Electrodes	43	60
Electric energy, Kilowatt-hours	3,280	4,600
Ferro-mangano-tungsten	715	1,000

MANUFACTURE OF TUNGSTEN SILICIDE.

This presents no special difficulties. A mixture of tungsten dioxide or anhydride, silica and carbon are charged into a resistance furnace. The reactions are as follows:

$$2\ WO_2 + 3\ SiO_2 + 10\ C = W_2Si_3 + 10\ CO.$$
$$2\ WO_3 + 3\ SiO_2 + 12\ C = W_2Si_3 + 12\ CO.$$
$$WO_2 + SiO_2 + 4\ C = WSi + 4\ CO.$$
$$WO_3 + SiO_2 + 5\ C = WSi + 5\ CO.$$

The mixture subjected to the electrothermic action should have a different composition from that indicated by the above reactions, the proportion of silica in particular needing to be higher because of its volatility and it being less easily reduced than tungstic acid or tungstic dioxide. In practice to obtain the silicide WSi it is necessary to use three parts of silica to four parts of tungstic acid; for the silicide W_2Si_3 there is needed at least five parts of silica to 4 parts WO_3.

The mixture should be agglomerated or briquetted to avoid loss by dusting from the gas disengaged.

If the furnace with two hearths in series is used an energy density of 125 to 140 watts per square centimeter of cross section of the electrodes and a voltage of 50 to 60 volts should be used. The lining of the furnace should be acid material; it may be made of WO_2 agglomerated with 6 per cent. of coal tar.

The tungsten silicides cast easily. When the furnace is tapped it is advisable to put into the runner a little borax or a mixture of pulverized glass and borax, to form a slag which will protect the metal from access of air.

INDUSTRIAL DATA ON THE MANUFACTURE OF TUNGSTEN SILICIDE.

Assume that the alloy WSi is to be manufactured from silica and an ore whose composition we have given before. The reaction will be written:

$$(3\ WO_3.1.5\ MnO.\ 1.5\ FeO) + SiO_2 + 24\ C = 3\ WSi + 1.5\ MnSi + 1.5\ FeSi + 24\ CO.$$

The materials reacting on each other and the products obtained may be tabulated as follows:

1,000 kg of ore.....$(1.5\ FeO.\ 1.5\ MnO.\ 3\ WO_3) + SiO_2$.
300 kg Silica.....$5\ SiO_2$.
288 kg carbon (360 coke) . 24 C.
886.5 kg silico-tungsten...$3\ WSi + 1.5\ MnSi + 1.5\ FeSi$.
672 kg Carbon monoxide..24 CO.

Electric Energy Required:

The calculation can only be approximated for the heat of formation and the heat of fusion of the complex silicide are not known. Nevertheless, the error in assuming this data will effect the final result less than 1 to 2 per cent.

HEAT OF REACTION.

Initial state	$MnWO_4$	1.50 × 338,000	507,000	Cal.
	$FeWO_4$	1.50 × 331,000	496,000	"
	SiO_2	6 × 179,060	1,077,600	"
	Total		2,081,100	"
Final state	WSi	3 × 20,000 (?)	90,000	Cal.
	MnSi	1.5 × 18,000	27,000	"
	FeSi	1.5 × 12,000	18,000	"
	CO	24 × 29,400	705,600	"
	Total		840,600	"
	Heat balance of the reaction		1,240,500	"

SENSIBLE HEAT IN PRODUCTS.

Total heat in the fused alloy at 2,100° 886.5 × 600 =	531,900	Cal.
Total heat in carbon monoxide $24\ (6.8 \times 1{,}600 + 0.0006 \times 1{,}600^2) =$	298,000	"
	829,900	"
Total heat requirement	2,070,400	"

Assuming a loss of 6 per cent. of the material charged the heat requirement will be per ton of alloy produced in the neighborhood

of 2,500,000 calories. If the thermal efficiency of the furnace is taken as 60 per cent. the above figure will correspond to an expenditure of 5,000 kilowatt-hours per ton of alloy produced.

The above calculation is made on the assumption that there will be no residual slag, which would be contrary to the fact, and it would be well to allow an expenditure of 5,400 kilowatt-hours to include the heat in the slag.

PRACTICAL DATA OF THE MANUFACTURE.

Materials used and produced.	Per ton of Ore.	Per ton of Alloy.
Ore: Wolframite containing 70 percent. WO_3	1,000 kg	1,200 kg
Silica	300	360
Coke	360	432
Electrodes	40	48
Electric energy	4,500 Kw-H.	5,400 Kw-H.
Silico-tungsten	835 kg	1,000 kg

MANUFACTURE OF METALLIC TUNGSTEN.

CHEMICAL PROCESSES.

The reduction of tungstic acid by hydrogen, or of tungsten chloride by sodium, and the amido-nitrate of tungsten by heat alone constitute laboratory processes which do not appear to be industrially feasible.

DELPINE'S PROCESS.

The only practical chemical process which can be economically operated is that of Delpine, which consists in heating to redness a mixture of tungstic acid or ammonium tungstate with pulverized zinc. The resultant product is a black mass, friable, and containing tungsten, zinc oxides and a little tungstic acid or dioxide resulting from incomplete reduction. The zinc oxide is removed by hydrochloric acid, and the powder is washed until the acid is removed. It contains 98.5 per cent. tungsten. On boiling the powder, after washing, with soda solution for several minutes and washing with cold water again, metal 99.5 per cent. pure is obtained.

The product is a gray powder, dense, takes on a metallic luster when burnished, burns in the air very easily, being completely oxidized to yellow WO_3. This powder may be fused in the electric furnace to massive tungsten, or utilized directly in the manufacture of tungsten alloys.

This process is used in Germany to manufacture metallic tungsten. The author used it in 1898, operating in an illuminating gas retort, heated by producer gas. The retort was filled three-quarters full of the mixture of tungstic oxide and zinc, agglomerated with tar and pressed into the form of small pellets by hand. The reduction took place easily at a temperature between 900 and 1,000° C.

ALUMINO-THERMIC METHOD.

Powdered aluminum easily reduces tungstic oxides:

$$WO_3 + Al_2 = W + Al_2O_3.$$
$$3\ WO_2 + Al_4 = 3\ W + 2\ Al_2O3.$$

The Goldschmidt process is very simple and its execution very easy. The crucible is furnished with a hood connected with a chimney, an intimate mixture of WO_3 and powdered aluminum is charged and ignited by the aid of a Bikford fuse which touches a little cartridge of barium dioxide. It is best to use a slight excess of WO_3 otherwise a small amount of the alloy WAl_4 forms, which dissolves in the tungsten and interferes with its metallurgical use. The slight excess of WO_3 forms aluminium tungstate of unknown composition, with the Al_2O_3, perhaps $Al_2(WO_4)_3$. This tungstate is insoluble in water.

Besides the slight loss in tungstic acid the greatest inconvenience in the alumino-thermic reduction is its great cost. For 184 grams of tungsten there is theoretically required 54 grams of aluminium; in practice there is used 1 part aluminium to 2½ parts tungsten. The cost of aluminium in powder is not below 70 cents per kilogram, making the cost of manufacture of tungsten certainly over 28 cents per kilogram, while the electro-metallurgical methods are very much cheaper.

ELECTROLYTIC PROCESSES.

The need of an electrolytic process has not been greatly felt, but it is possible that later they may become of importance. A process similar to that proposed by the author for molybdenum, the electrolysis of the double chloride of tungsten and sodium may solve the question, using as anodes soluble plates of cast tungsten, and as cathodes powdered tungsten pressed or hammered

together. The double chloride of tungsten and sodium can be made in the same manner as the corresponding compound of molybdenum. Electrolysis gives a porous pyrophoric mass which must be cooled before being handled, and should be remelted in the electric furnace.

The fused product may be directly obtained by using as cathode a bath of lead which remains liquid until the tungsten content reaches 15 percent. The alloy may then be heated in the electric furnace until the lead volatilizes, leaving the tungsten behind.

The author tried to obtain melted tungsten by the electrolysis of tungsten dioxide dissolved in fused calcium fluoride. The anodes were carbon and cast tungsten and the cathode of powdered tungsten. To obtain liquid metal required such high current density that the calcium fluoride partially volatilized, while the phenomenon of calcifaction makes the running very irregular.

SILICO-THERMIC PROCESS.

The induction furnace is used into which is charged tungsten silicide either run in liquid or manufactured in the same furnace. The slag being removed, a mixture of tungstic acid and lime or calcium tungstate or an alkaline tungstate is thrown on its surface. If an alkaline tungstate is used vapors of sodium sublime as Na_2O as an impalpable powder, which is easily absorbed by the respiratory organs and become dangerous to the workmen. A mixture of tungsten dioxide and lime may also be used. The reaction between the silicide and tungstic acid is written:

$$W_2Si_3 + 2\,WO_3 + 3\,CaO = 4\,W + 3\,CaSiO_3.$$

Naturally, the induction furnace should be run at a high enough temperature to keep the tungsten well fused. The only lining which will resist this temperature and the corrosive action of the silica is pure magnesia or pure strontia. The energy density should not be less than 1,200 to 1,500 watts per cubic decimeter of metal contained in the channels of the furnace.

MANUFACTURE OF NICKEL-TUNGSTEN.

This may be done also to the induction furnace either from tungsten silicide by means of nickel oxide or from nickel silicide by tungsten dioxide or trioxide, with the addition of lime.

Alloys of very different tungsten content may be obtained between WNi_3 carrying 50 percent. tungsten to WNi with 75 percent. tungsten. These alloys are difficultly fusible and the furnace must be run with a high energy density, such as 1,100 watts per cubic decimeter of metal.

It is possible to manufacture also to start with neutral tungstate of nickel by fusing sodium tungstate with nickel chloride and sodium chloride. On washing the mass, blackish green crystals are obtained which on reduction in the electric furnace will give the alloy WNi containing 3 per cent. carbon.

MANUFACTURE OF CHROME-TUNGSTEN.

A solution of chromium sulphate and a solution of neutral sodium tungstate are made and mixed hot. This forms a green precipitate of neutral cromium tungstate only slightly soluble in water:

$$Cr_2(SO_4)_3 + 3\ Na_2WO_4 = 3\ Na_2SO_4 + Cr_2(WO_4)_3.$$

The solution is decanted and the precipitate washed and dried.

From this compound the chromium-tungsten alloy may be reduced and refined by the use of the same compound; or if it is desired to have a larger proportion of tungsten in the alloy it is reacted upon by tungsten silicide according to the reaction:

$$Cr_2(WO_4)_3 + 2\ W_2Si_3 + 6\ CaO = W_7Cr_2 + 6\ CaSiO_3.$$

This alloy contains 7 to 8 per cent. of chromium, a proportion much sought for in the manufacture of high-speed steels. It is possible to dispense with the manufacture of chromium tungstate and to act directly upon tungsten silicide by chromium oxide. It is also possible to react upon 50 per cent. ferro-silicon with chromium tungstate thus:

$$3\ FeSi_2 + Cr_2(WO_4)_3 + 6\ CaO = CaSiO_3 + Fe_3Cr_2W_3.$$

There is obtained a ferro-chrome-tungsten containing 12 per cent. chromium and 50 per cent. tungsten.

If the induction furnace is used, an energy density of 1,100 to 1,200 watts per cubic decimeter of metal in the furnace must be used.

TUNGSTEN IN THE METALLURGY OF STEEL.

Tungsten plays an important rôle in the manufacture of the special steels. It forms a number of definite compounds with iron, amongst which have been observed Fe_3W, Fe_3W_2, FeW_2, and Fe_4W. The metal was formerly and is now introduced into the steel in the form of powder, but this method is accompanied by considerable loss and makes a steel of very variable composition. The use of 30 to 80 per cent. ferro-tungsten is coming into use more and more. In the electrical production of the special steels the use of pure tungsten will become most general.

THE RÔLE OF TUNGSTEN IN STEEL.

Tungsten increases very markedly the hardness of steel, and gives to it a very fine grain and velvety appearance. Quenching gives to a tungsten steel a very close grain and silky appearance on fracture. Quenching lowers the tensile strength of these steels, but this property is regained by heating to a high temperature.

Some of the observations which follow have been taken from the communication of Guillet to the Metallurgical Congress at Liege in 1905. Tungsten, like carbon, lowers the melting point of steel. According to Otto Bohler, the lowering is proportional to the quantity of tungsten introduced, but in a measure less than the effect produced by a corresponding quantity of silicon or carbon. The lowering of the melting point is according to the law of Raoult inversely proportional to the molecular content. In any case this lowering of the melting point is only produced between certain limits of tungsten content, for when this exceeds a certain limit the melting point increases markedly. Non-carburized tungsten raises the points of transformation; carburized tungsten added to steels of high carbon content, lowers them a little. The critical points are notably displaced depending on the temperature at start and the rate of cooling.

Osmond has made the following observations on steels of 0.42 per cent. carbon and 6.25 per cent. tungsten. If it is cooled below 920 there is noticed two neighboring unlike critical points; the first between 690 and 680°, the second about 650°. The cool-

ing curve is analogous to that of ordinary steel of the same carbon content.

When the temperature has been raised to about 1,015° the first point remains fixed in its place (670-660°), but the second drops to between 525 and 515°, that is about 130°.

If the temperature is raised to 1,210° the first point drops sharply and rejoins the second at about 500°. Following the method of Roberts-Austen, Otto Bohler has shown that a steel of 0.85 per cent. carbon and 7.70 per cent. tungsten has two critical points, 710 and 550°; the first only appears if the initial temperature does not exceed 1,100°, and the second only after it has exceeded 1,000°. Between these two temperatures the two points are observed. Prolonged heating to a given temperature has the same effect on the critical points and the cooling curve as a briefer heating to a higher temperature.

METALLOGRAPHY.

If steels of 0.2 per cent. carbon content are considered, and with 0 to 10 per cent. tungsten, they have the same constitution as carbon steels, except that the pearlite is better defined and even at a slight enlargement alternate lamina of ferrite and cementite are perceived.

With 10 per cent. tungsten, there can be seen lamina and points of extreme fineness appearing white after etching with picric acid. This is a double carbide and is encountered in all steels up to 40 per cent. tungsten.

In steels containing 0.8 per cent. carbon perlite is found between 0 and 5 per cent. tungsten. As soon as the tungsten content attains 5 per cent. the double carbide appears. Sometimes it is in extremely small points, generally it is in free filaments, sometimes even in fine grains where it has escaped mechanical treatment and may then be even in crystal form.

To sum up the micrographical structure of the steels we have the following table:

Microstructure.	Steel with 0.2% Carbon.	Steel with 0. 8 % Carbon.
Perlite	0 to 10% tungsten	0 to 5% tungsten
Double Carbide in white filaments or grains	W > 10%	W > 5%

The special constituent which appears in the carburized steels is the double carbide whose properties are much like those of cementite. It appears in relief on polishing and sodium picrate in alcoholic solution colors it black. Its formation in the perlitic steels is assisted by prolonged heating.

PROPERTIES OF TUNGSTEN STEELS.

Tungsten steels have been the subject of remarkable researches on the part of Hadfield, who presented the same in an interesting memoir to the Iron and Steel Institute September, 1903. The researches of Guillet correspond with those of Hadfield in the following conclusions:

1. Perlitic steels have an ultimate strength increasing with the tungsten content. The elastic limit does not seem to increase as rapidly. The contraction and elongation decrease slightly. They are not more brittle than carbon steels, and their hardness is generally greater than that of ordinary steels of the same carbon content.

2. Steels containing the double carbide have their ultimate strength increased by increase of carbon, but this strength does not tend to increase with the tungsten content. The elastic limit is relatively low. The elongation and contraction are very slight. They are brittle steels. Their resistance to shock is constant whatever may be their tungsten and carbon content. Finally, they have an increasing hardness with increase of carbon content.

INFLUENCE OF QUENCHING.

Quenching has the same effect on perlitic steels as on carbon steels.

On steels containing the double carbide, quenching at 850° produces an extremely fine martensite and leaves a part of the carbon undissolved, at least when the tungsten content is high. The higher the temperature of quenching above 850° the smaller is the quantity of carbide present. After quenching, these steels have an ultimate strength and elastic limit and hardness far greater than in the annealed state.

MAGNETISM.

The experiment of Curie show that the magnetic transforma-

tion points are very little affected by the tungsten content and are slightly higher than in ordinary steels of the same carbon content.

HARDNESS.

According to Bohler, the hardness both before and after quenching, is sensibly constant. The hardness before quenching varies from 1 to 1.5 and after quenching 2.1 to 3.3.

CHEMICAL ANALYSIS OF TUNGSTEN

CHARACTERISTIC REACTIONS BEFORE THE BLOW-PIPE.

In the oxidizing flame of the blow-pipe, tungstic acid remains unaltered; it blackens in the reducing flame, in consequence of the transformation of WO_3 to WO_2, which remains infusible.

With borax in the outer flame, it gives a clear and colorless bead; if the quantity of WO_3 is relatively large the bead is yellow hot and enamel white on cooling.

In the reducing flame the bead is colored yellow or yellowish brown. This coloration is accentuated on charcoal or with a grain of tin.

Salt of phosphorus dissolves tungstic acid in the outer flame and gives a clear, colorless yellow bead with an excess of acid; in the reducing flame, the bead becomes greenish hot and blue on cooling. It assumes a blood red color if the tungstic compound is ferruginous; but it becomes blue again on addition of a small quantity of tin.

On a platinum wire in the oxidizing flame, sodium carbonate dissolves tungstic acid and gives a clear, dark yellow glass, which becomes crystalline and white or yellowish cold. Heated on charcoal with a little sodium carbonate, tungstic acid is reduced and transformed into metallic tungsten. In the presence of an excess of sodium carbonate, a yellow glass is formed which has a metallic lustre and which soaks into the charcoal.

Bunsen, on submitting tungstic acid to pyrognostic analysis, has given the following reactions as characterizing tungstic acid:

Heated in the reducing flame of the Bunsen burner with sodium carbonate on charcoal, compounds of tungsten give with difficulty a gray metallic powder.

If a portion of the substance is mixed with sodium carbonate

and a small quantity of potassium nitrate, and if heated in a spiral made of platinum wire in the hot portion of the flame of a burner, there is obtained a white or colorless melt. On dissolving it in water and absorbing this liquid by means of narrow strips of Berzelius paper a tungstic compound gives the following reactions:

No coloration with ferrocyanide after addition of hydrochloric acid.

Blue coloration with protochloride of tin.

Blue or greenish coloration, by successive reactions of ammonium sulphide and hydrochloric acid.

CHARACTERISTIC REACTIONS IN THE WET AND DRY WAY.

Compounds of tungsten may always be converted into tungstic acid or alkaline tungstates.

Tungstic acid is characterized by its yellow color, its insolubiiity, and its resistance to reagents. It is insoluble in the acids, except in hydrochloric acid if it has not been calcined.

Hydrofluoric acid dissolves it slowly.

When tungstic acid is fused with an alkaline bisulphate one obtains, after washing, a mass of white alkaline tungstate which is soluble in pure water and insoluble in the acid.

Tungstic acid which has not been calcined is easily soluble in ammonia, free alkalies and carbonates.

Calcined tungstic acid must be fused with alkaline carbonates or alkalies in order to be brought into solution.

On acidifying the solution of an alkaline tungstate, a white precipitate is formed in dilute solution or a yellow precipitate if the solution is concentrated.

These reactions may be different if one has to do with a metatungstate, which is not precipitated cold by acids, but only after prolonged boiling.

In this case it is necessary to transform first to an alkaline tungstate by an addition of an excess of alkali to the metatungstate.

The presence of tungstic acid may be masked by the presence of phosphoric, silicic, or boric acid, etc., forming compound acids possessing special properties.

In the presence of hydrogen sulphide, acid solutions are col-

ored blue and neutral or alkaline solutions yellow. On addition of dilute acid, a precipitate of tungsten sulphide results.

Ammonium sulphide gives no precipitate in a neutral solution; in an acid solution it precipitates tungsten sulphide, which is soluble in an excess of the reagent.

Soluble alkaline-earth salts and salts of zinc and lead give a white precipitate with alkaline tungstates. Mercurous salts give a clear, yellow precipitate.

Protochloride of tin gives a yellow precipitate which becomes blue when heated in the presence of hydrochloric acid.

Metallic zinc in the presence of hydrochloric acid gives a fine, blue coloration, then a blue precipitate. This reaction is also produced in the presence of phosphoric acid. M. Defacqz has suggested a very convenient reaction to test for tungstic acid. The compound is treated with four or five times its weight of potassium bisulphate and a few drops of sulphuric acid and heated gently. After cooling, a drop of carbolic acid is added. This gives an intense red color. With hydroquinone, the color is an amethystine-violet.

DETERMINATION OF TUNGSTEN.

For this chapter we have borrowed from Carnot's treatise on analysis and various publications.

The determination is made in the state of:

WO_3, of which one hundred parts correspond to 79.31 of W.

$CaWO_4$, of which one hundred parts correspond to 80.55 of WO_3 or 63.89 of W.

$CdWO_4$, containing 74.57 per cent. of WO_3, or 60.52 per cent. of W.

It may also be determined volumetrically by reduction.

Tungstic Acid and the Alkalies.—Either the acid alone or the acid and the alkali may be determined.

1. The solution may contain sodium tungstate and sodium carbonate; this is nearly neutralized by nitric acid, and the carbonic acid driven off by heat.

A very dilute, slightly alkaline liquid is thus obtained, to which an excess of calcium nitrate is added and the solution boiled for several hours; then the precipitate is allowed to settle com-

pletely. It is somewhat gelatinous and contains all the tungstic acid in the condition of calcium tungstate with a little calcium carbonate. This is easily and completely washed by several decantations, boiling each time. This is filtered and dried at 100°, the precipitate separated from the filter paper which is burned, and the ashes added.

The product thus obtained is treated cold by dilute acetic acid for several hours, until small bubbles of carbonic acid gas are liberated. The carbonate is dissolved while the tungstate is not attacked. This is washed upon the filter with dilute acetic acid. It is dried, the paper is burned separately, the whole is calcined at a dull red heat and weighed as $CaWO_4$.

The determination may also be terminated in the following manner: The dried precipitate and the ashes from the filter paper are treated in a porcelain capsule with nitric acid, evaporated to dryness, maintained several hours slightly below 100° and taken up again in dilute nitric acid. (Same operation to render the silica of a silicate insoluble).

Tungstic acid remains insoluble. It is washed with boiling water, ignited and weighed with the ashes of the filter paper, which has been burned separately. It is necessary to heat it in the oxidizing atmosphere of a muffle to obtain the yellow acid. If it becames slightly green, a partial reduction is evident. Treat with nitric acid and heat gently to redness in an oxidizing atmosphere in order to weigh only the yellow WO_3 whose composition is exact.

The tungstic acid may be precipitated by mercurous nitrate after having neutralized as exactly as possible the alkali present with nitric acid. A few drops of ammonia are added until a black precipitate of an amido compound of mercury begins to form. This precipitate is washed with boiling water, dried at 100°, the filter paper burned separately and the whole ignited in a muffle. The determination of WO_3 is exact.

To determine the alkali in a solution which contains mercurous nitrate in excess, a rapid current of hydrogen sulphide is passed into it which precipitates the black Hg_2S. This precipitate is washed with pure water, the hydrogen sulphide driven out by boiling, the liquid is filtered, evaporated to a small volume and sulphuric acid added to form a sulphate. Evaporate to dryness,

ignite and weigh the neutral sulphate in a previously tared platinum crucible.

The alkali can also be weighed as a carbonate by adding to the solution after freeing from tungsten, oxalic acid. Evaporate and calcine gently to volatilize the mercury.

Other Methods.—According to the experiments of H. Smith and H. Bradbury, the determination of tungstic acid could be made as $CdWO_4$, a very fine precipitate which does not pass through the filter paper. It is soluble in acids and ammonia, but becomes insoluble after calcination. A slight excess of nitric acid is poured into the solution. This is neutralized by ammonia, then cadmium nitrate is added, boiled, filtered, dried, calcined, washed with dilute acid and ignited and weighed as $CdWO_4$.

Some chemists have used lead acetate as a precipitant. This is poured into the alkaline solution after neutralization with acetic acid. Lead tungstate is precipitated, washed with ammonium nitrate, and allowed to digest with ammonium sulphide. The sulpho-salt of tungsten is then filtered, evaporated to dryness and calcined lightly. It is then oxidized by nitric acid, calcined the second time and weighed as WO_3.

The tungstic acid may be separated from the alkalies by acidifying the solution with sulphuric acid, evaporating to dryness and gently igniting the residue. By taking up in hot water and washing well the alkaline sulphate is all removed, leaving only tungstic anhydride, which is ignited and weighed.

Tungstic Acid and the Alkaline Earths.—As mentioned above, calcium tungstate may be treated with nitric acid, evaporated to dryness, heated for some time at about 100° and taken up in the same acid. Tungstic acid remains insoluble and can be precipitated in the solution containing only lime and nitric acid. It is easy to determine the alkaline earth.

A different procedure consists in mixing one part of tungstate with six parts sodium carbonate and fusing in a platinum crucible. This is dissolved in water, which leaves the calcium carbonate as an insoluble residue. This is washed well, ignited and weighed as CaO. By difference the tungstic acid is obtained, which would otherwise be precipitated by mercurous nitrate in the neutralized solution.

This method may also be used to separate tungstic acid from

the oxides of Fe, Mn, Ni, Co, Pb; hence is applicable to the analysis of wolframite.

Tungstic Acid and Silicic Acid.—When the silica is present as quartz in the substance under consideration, the employment of hydrochloric acid or aqua regia, results in an insoluble mixture of tungstic acid and quartz, which is very easily separated by treating with ammonia, which dissolves only the tungstic acid.

But several difficulties are encountered in the analysis of the compounds called silico-tungstates, containing the two acids in combination with bases; let us assume with alkali.

The procedure is similar to the separation of silica and alkali, treatment with hydrochloric acid, evaporation to dryness, continued heating at 100°, and resolution in the acid. The insoluble portion, well washed, contains tungstic and silicic acids. This is washed, calcined and weighed.

We have then a combination of the two acids; the tungstic acid cannot be completely dissolved by means of ammonia. It is necessary to destroy the combination by submitting the mixture to the action of pure, dry hydrogen at a bright red heat for two hours, in order to reduce tungstic acid to metallic tungsten. After cooling in the hydrogen, it is treated by means of aqua-regia at about 100°; this is washed with boiling water, the reformed tungstic acid dissolved in ammonia and separated from the silica. The solution is evaporated gently to dryness, the residue calcined and weighed as tungstic anhydride. The silica is calculated by difference because of losses due to the carrying out by the current of hydrogen, which are to be feared.

One can also destroy the combination of silicic acid with tungstic acid by heating the mixture in a current of hydrogen sulphide to a dull redness, in order to form tungsten sulphide, WS_2, and then taking up in aqua-regia.

The other method is based on the volatilization of the silica in the form of silicon fluoride. After having weighed the mixture of silica and tungstic acid it is treated with hydrofluoric and sulphuric acids. The residue of tungstic acid obtained after evaporation and calcination is weighed directly. The determination is not only more rapid, but more sure than the method preceding, as the silica is not insoluble in ammonia in the preceding case.

Finally, one can fuse the mixture in potassium bi-sulphate and

take up in water. The silica remains insoluble while the tungstic acid is dissolved. The precipitation can be completed by mercurous nitrate.

Tungstic Acid and Titanic Acid.—The sample taken may contain a mixture of the two acids and should then be fused for 20 to 30 minutes in a platinum crucible with 7 to 8 parts of a mixture of potassium nitrate 4 parts and potassium carbonate 1 part. The fused mass is dissolved in water, evaporated to dryness on a steam bath, then the insoluble titaniferous residue is washed first with water by decantation and finally on the filter, the wash-water containing ammonium nitrate. Tungstic acid is precipitated from the solution by means of mercurous nitrate. The insoluble residue of titanic acid is fused with potassium bisulphate, the fused mass dissolved in water and the titanic acid determined in this solution in the ordinary manner.

Titanic, Tantalic, Columbic and Tungstic Acids—In a number of minerals a mixture of these four acids is found. When the mixture has not been calcined one can separate the tungstic acid by digestion in ammonia with hydrogen sulphide; the other acids remain insoluble. The sulpho-salt is evaporated to dryness, the residue is moistened with nitric acid and calcined.

The solution of tungsten is not entirely insured by hydrogen sulphide after the mixture has been submitted to calcination. It is often convenient to fuse with three parts of sulphur and three parts of sodium carbonate. The tungsten alone dissolves and is taken up in water. This is evaporated to dryness, decomposed by hydrochloric acid, boiled with aqua regia, after which the insoluble tungstic acid is collected and washed.

Tungstic Acid and Tin Dioxide.—One can separate these two by reduction at a red heat in hydrogen. The product is metallic tin and tungsten dioxide WO_2. This is now attacked by hydrochloric acid and which dissolves out the tin when heated; one can then precipitate the tin by a current of hydrogen sulphide. The residue when heated in the air is transformed into tungstic acid, which is weighed. One must avoid heating in hydrogen so strongly as to produce metallic tungsten which will alloy with the tin and remain insoluble in the hydrochloric acid. One can also heat to dull redness in a current of hydrogen sulphide which produces SnS and WS_2; on treating with hydrochloric acid the

tin sulphide dissolves and the tungsten sulphide remains unattacked. This can be weighed in the form of sulphide, or after oxidation in the form of WO_3.

The separation of WO_3 and SnO_2 can be made in a satisfactory manner by fusing the mixture with a large excess of potassium cyanide. This is then taken up in water, dissolving out the alkaline tungstate with the other potassium salts, while the tin is found as metallic buttons which can easily be weighed after washing and drying.

VOLUMETRIC ESTIMATION OF TUNGSTIC ACID.

The reduction of tungstic acid by zinc in a hydrochloric acid solution results as a final product in the salt tungstous oxide, WO_2. From this may be established a volumetric method (Von der Pfordten).

The alkaline tungstate, containing not more than 0.1 gram of tungstic acid, is treated with 70 to 80 c.c. of 27 per cent. hydrochloric acid, then 15 grams of zinc is added, and the whole set on a steam bath. When the liquid has become red, it is cooled and decanted into a porcelain capsule which contains a measured amount of potassium permanganate, together with manganous sulphate and sulphuric acid. Then dilute to a liter and take an aliquot part of the solution and run in a solution of ammonium ferrous sulphate until the permanganate is decolorized. This determines the amount of permanganate required to transform the WO_2 to WO_3.

It is best to standardize the solutions against a known amount of pure WO_3.

ANALYSIS OF SCHEELITE.

Two grams are heated with nitric acid. When the attack seems complete, evaporate to dryness and maintain for twenty-four hours at 100°, and then take up in the same acid. All the lime and a portion of the iron and manganese are dissolved. The tungstic acid, the silica and the rest of the iron and manganese form an insoluble residue, which is taken up in aqua regia containing an excess of hydrochloric acid, boiling for several hours. The new solution thus obtained contains the second part of the iron and manganese, while the residue contains the tungstic acid and the silica.

The residue is washed with boiling water and is then treated with ammonia, which dissolves the tungstic acid and leaves the quartz, which can here be weighed.

The ammoniacal solution, evaporated to dryness, leaves a residue which is transformed into tungstic anhydride on calcination. The nitric acid solution is evaporated to dryness, heated to 180°; this decomposes the nitrates of iron and manganese. These are taken up by a saturated solution of ammonium nitrate, heated to about 100°. All the lime is thus dissolved and again precipitated by ammonium carbonate. It is finally determined as CaO.

The oxides of iron and manganese remain insoluble in the ammonium nitrate and are dissolved by hydrochloric acid and added to the solution which contains the rest of the metallic oxides. The hydrochloric acid solution containing all the oxides of iron and manganese is precipitated by oxygenated water and ammonia in great excess while boiling. The iron and manganese are precipitated together. The precipitate is washed, dried, calcined and weighed as $Fe_2O_3 + Mn_3O_4$; the manganese is usually in small quantity and is not in general separated. They could also be determined by methods given further on.

ANALYSIS OF WOLFRAMITE.

A. Attack by aqua regia.—One to two grams of the mineral, finely pulverized, are treated by aqua regia formed of four parts of hydrochloric acid and one part nitric acid, using a large flask which can be agitated frequently and boiled without fear of loss. The attack takes place slowly and forms a yellow, gelatinous, tungstic acid, which sticks to the sides of the flask and covers the mineral itself. It is therefore necessary to agitate the flask almost continuously. Violent bumping of the solution will otherwise ensue. It is necessary to heat strongly and to continually renew the acids. An appreciable loss of the chlorides of iron and manganese is to be feared; this can be avoided by employing small quantities of acid at a time and agitating and decanting frequently.

When the attack appears to be complete, boiling water is poured into the solution and the whole is allowed to stand. The clear liquid is decanted, the residue washed by decantation two or

three times with water strongly acidified with hydrochloric acid, boiling each time with acid before adding the water. Finally, the precipitate is filtered out and washed on the filter and in the flask with boiling water. It is necessary to prolong the washing until the complete elimination of iron and manganese has taken place, which otherwise would partially pass with the tungstic acid into the solution in ammonia.

Ammonia is poured into the flask along the sides where the tungstic acid adheres to them. Then the ammoniacal liquor is poured through a filter, the residue washed a few times with dilute ammonia, the filter is dried and burned. The residue is unattacked wolframite, with a little quartz mixed with it. One may have a small residue, at most two centigrams, but if more, it should be again attacked with aqua regia.

The ammoniacal solution is evaporated to dryness and the salt, $(NH_4)_2WO_4$, is decomposed by heat. This residue is mixed with a few drops of hydrofluoric and sulphuric acids, evaporated to dryness and calcined, the tungstic anhydride, WO_3, being weighed.

The acid solution resulting from the attack is neutralized, drop by drop, to almost exactness by ammonia and ammonium carbonate and ammonium acetate added to excess, the whole being finally boiled. All the iron is thus precipitated. This is redissolved in nitric acid and reprecipitated by ammonia and weighed as Fe_2O_3. The manganese is precipitated with bromine. This is calcined and determined in the condition of Mn_3O_4. If lime and magnesia are present, they are found in the filtrate and may be precipitated successively by ammonium oxalate and sodium phosphate.

TANTALIFEROUS WOLFRAMITE.

The mineral, very finely pulverized, is attacked by hydrochloric acid to which a little nitric acid has been added and the whole boiled. Dilute with water, decant and wash the residue by decantation. The insoluble residue is dissolved in ammonia and hydrogen sulphide. Decant and wash with water saturated with hydrogen sulphide. A slight residue, colored black by sulphide of iron, remains, which, on treating with hydrochloric acid, becomes white. It consists of a little unattacked wolframite

and the tantalic acid. The hydrochloric acid solution is added to the first, containing the iron, manganese, lime and magnesia. The attack is completed by fusing the residue with potassium bisulphate, then treating with boiling water and taking up the residue in ammonium sulphide, which dissolves the rest of the tungsten.

The residue, colored black by sulphide of iron, is purified by hydrochloric acid, which leaves the tantalic acid insoluble combined with sulphuric acid. By calcination at bright redness, Ta_2O_5 remains.

The hydrogen sulphide solution is evaporated to dryness, the dry residue moistened with a few drops of nitric acid, evaporated to dryness again, and calcined to WO_3

The acid solutions containing the metals are combined, the iron and manganese are precipitated by ammonia and hydrogen sulphide, and the solution used for the determination of lime and magnesia. The sulphide precipitate is redissolved, oxidized. precipitated by ammonia, and the precipitate weighed together as $Fe_2O_3 + Mn_3O_4$; then the two metals are separated.

B. Fusion with alkaline reagents.—The decomposition of wolframite is much more easily made by dry methods, either by the use of a mixture of alkaline carbonates or by calcium carbonate and sodium chloride (F. Jean).

1. A gram of wolframite, finely pulverized, is mixed with 3½ grams of sodium carbonate and as much potassium carbonate; the whole is kept in complete fusion for about twenty minutes. The platinum crucible is inclined in all directions, in order to insure the solidification of the fusion against the sides of the same and yielding the greatest surface possible. It is then easy to separate the melted mass, after cooling from the crucible, by slightly deforming the latter. The fused mass thus obtained is treated with water and a little alcohol added and the whole heated to boiling to precipitate the manganese. Finally, a few grams of ammonium carbonate are added and the solution saturated by a current of carbon dioxide.

The iron, manganese and a large part of the silica remain insoluble. The soluble alkaline tungstate is separated by filtration and the elements remaining in the residue determined separately.

The alkaline solution is slightly acidified with nitric acid, then it is boiled to remove carbonic acid. This solution is then rendered slightly alkaline by the addition of potassium or sodium carbonates and precipitated by boiling with a saturated solution of mercurous nitrate. The precipitate is washed with water containing a little mercurous nitrate and carefully dried. It is then separated as much as possible from the paper, which is burned separately under a hood, with a good draft. The precipitate is added to the ashes from the paper and heated very slowly and progressively, finally strongly. After cooling and weighing, the precipitate is mixed with a few cubic centimeters of hydrofluoric acid containing a few drops of sulphuric acid, and weighed again after evaporation and calcination. The difference in weight represents a small amount of silica which was carried along and escaped precipitation by the carbonic acid.

2. *Method of F. Jean.*—A gram of finely pulverized wolframite is mixed with 500 milligrams of calcium carbonate and 500 milligrams of pure salt and heated to bright redness. The mass is taken up in concentrated hydrochloric acid and the bottom of the crucible heated, causing easy separation of the mass. After complete disintegration, dilute with water and the tungstic acid, and a part of the silica will remain insoluble. Filter, wash and separate as indicated above. The hydrochloric acid solution contains the bases which are determined by general methods. This method is of advantage for the special determination of tungsten and is very rapid.

WOLFRAMITE AND CASSITERITE.

Rapid Methods for Determination of Tungsten and Tin.

Take one gram of the finely powdered mineral and mix with eight grams of a mixture of sodium and potassium carbonates. After fusing one hour, allow to cool, and treat with hot water. Wash to a bulk of 200 cubic centimeters, filter, and pour into a mixture of 60 c.c. of hydrochloric acid and 20 c.c. concentrated nitric acid. Evaporate to dryness and take up in water containing 10 per cent. hydrochloric acid and 10 per cent. ammonium chloride. Boil and filter. The residue, containing the tungstic acid, the oxide of tin and the quartz, is treated with hot ammonia to dissolve the tungstic acid. As there may also be a little iron

and manganese present, the solution is acidified with hydrochloric acid, instead of simple evaporation of the ammoniacal solution, to dryness, the residue by this treatment containing a less proportion of metallic oxides. After filtration and calcination, the precipitate is weighed as WO_3.

The residue, insoluble in the acids and ammonia, is treated with hydrochloric acid, washed, dried and fused with potassium cyanide to obtain metallic tin.

Cremer Method for the Determination of Tungstic Acid.

Fuse one gram of the finely powdered mineral in a porcelain crucible with 10 to 12 grams of potassium bisulphate. Heat slowly at first, then raise the temperature progressively, in order to maintain molten, and finally keep at a red heat for ten minutes. Then plunge into the crucible a piece of platinum, which serves, after cooling the mass, to lift out the cake. Plunge the platinum to which the cake adheres into a solution of boiling hydrochloric acid of specific gravity 1.056, and see that all particles remaining in the crucible are also added to the acid solution, introducing the crucible if necessary.

Continue boiling the solution, take out the crucible and platinum, dilute with hot water, and boil for fifteen minutes more. Add a few c.c. of a concentrated solution of cinchonine in hydrochloric acid, and, after a few minutes boiling, the yellow precipitate is allowed to settle. Filter and wash with water containing a little cinchonine.

The filter and its contents are placed in a porcelain crucible, dried, and heated gradually to a bright redness. Cool and weigh. Dissolve this precipitate in an excess of ammonia, boil, filter, and wash with boiling water, dry and calcine again and weigh. The difference between the two weights is tungstic acid.

Bollnheimer Method for the Determination of Tungstic Acid.

One or two grams of mineral are fused in a nickel crucible with four grams of peroxide of sodium and three grams of caustic soda, the latter in a single piece, which should remain at the bottom of the crucible, which should be heated gently in a Bunsen flame until the whole mass softens, and then the flame increased until the contents of the crucible become fluid, and

finally until the crucible begins to redden. The wolframite is completely dissolved by this method, while tin minerals remain unattacked in part.

After solidification, the crucible, still warm, is placed in a beaker containing water, and the solution thus obtained is diluted to 250 c.c. in a flask. If manganate is present, the green color should be made to disappear by the addition of hydrogen peroxide. When it is cold, the flask is filled with water to the mark and half the solution is filtered.

Twenty grams of ammonium nitrate are added, which will transform all the caustic soda to nitrate and liberate ammonia with a strong excess of ammonia. After solution, the same is allowed to stand to precipitate the silica and stannic acid. The necessary amount of magnesium nitrate is added in small quantities to precipitate the phosphoric and arsenic acids if they are present. The magnesium salt should not be added before taking out the silica and stannic acids, or tungsten will be carried down in the precipitate.

It is necessary to employ ammonium and magnesium nitrates, because the excess of chlorides and sulphates present preclude the employment of mercurous nitrate. After having stood six to twelve hours, the precipitate is filtered, washed, first with ammonia and then with water. The filtrate is rendered slightly acid with nitric acid after cooling, as acidification sets free a considerable amount of heat. Then, 20 to 30 c.c. of a solution of mercurous nitrate are added. To prepare this solution, heat gently 200 grams of mercurous nitrate and 20 c.c. of nitric acid with a little water; dilute to a liter and add mercury. A few hours later add ammonia, until the solution is only slightly acid, and allow to stand until the solution above the dark precipitate is clear.

The precipitate is then filtered and washed with water containing mercurous nitrate. If the directions detailed above have been carefully followed, the filtration, and even the washing, are easily accomplished.

The precipitate is then calcined over a Bunsen flame and then over a blast lamp to constant weight.

In the presence of molybdenum, which is rarely the case, considerable time is necessary to completely volatilize this metal

and to attain constant weight. The time of this operation may be lessened if, before heating strongly the first time, a little ammonium chloride is added. Heat strongly again in a covered crucible, finally in an open crucible.

Boretraeger Method for the Determination of Tungstic Acid.

The author recommends the following rapid method as sufficiently exact for current practice. As the greater part of the tungstic minerals are brown in color, we are generally concerned with a mangano-ferrous tungstate mixed with impurities. This combination may contain, at most, 76 per cent. of tungstic acid, so that there are three parts of tungstic acid with each part of oxide. Therefore, fuse one gram of finely-powdered mineral with 10 grams of dry sodium carbonate and maintain in fusion one hour. The fused mass is dissolved, filtered, and the residue calcined. By deducting the weight of this residue from 100, one obtains within 5 per cent. of the tungstic acid content. When it is desired to obtain the tungstic acid content more exactly, it is convenient to precipitate in the following manner: Fuse for an hour one gram of finely-powdered mineral with 10 grams of dry sodium carbonate. Dissolve in hot water, dilute to 250 c.c., measure out 100 c.c. (0.4 gram mineral), and add to a mixture composed of 15 c.c. concentrated nitric acid and 45 c.c. concentrated hydrochloric acid. Evaporate to dryness, take up the residue in 1,000 c.c. water containing 100 grams hydrochloric acid and 100 grams of ammonium chloride. The residue containing the tungstic acid, silica and tin oxide is treated with ammonia. The solution is added to the mixture of acids and again evaporated to dryness. Tungstic acid thus obtained is pure and can be weighed after calcination.

Fretschle Method for the Determination of Tungstic Acid.

Half a gram of well-pulverized mineral is placed in a 25 c.c. porcelain capsule and treated with a mixture of hydrofluoric and hydrochloric acids. Heat to boiling for an hour, adding, from time to time, a mixture of the acids. When all the mineral has dissolved, concentrate by evaporation to drive off the fluoride of silicon which has been formed, taking care to avoid loss by spattering. The residue, after this evaporation, is treated with

a mixture of 20 c.c. hydrochloric acid and 8 c.c. nitric acid to drive out the last traces of hydrofluoric acid. Under these conditions, the tungsten fluoride is transformed first into chloride, which is later precipitated by the nitric acid as tungstic acid. Add 50 c.c. water and heat for a half-hour to complete the precipitation of the anhydrous tungstic acid. After standing filter, wash with hot water, dry and calcine the precipitate at a red heat. Weigh as WO_3.

DETERMINATION OF TUNGSTEN IN STEEL.

Method of Ibotson and Brearley.

Treat 5 grams of drillings with 100 c.c. of hydrochloric acid at boiling temperature. This dissolves the iron without attacking the tungsten. When the attack is nearly complete, add nitric acid, drop by drop, to oxidize the tungsten. Boil until all the tungstic acid is precipitated, add hot water and boil again, finally allowing the tungstic acid to settle in the hot solution. Filter and calcine the precipitate and treat with hydrofluoric acid to dissolve the silica. Separate the traces of oxide of iron from this precipitate by fusion with sodium carbonate, dissolve, filter, and precipitate with mercurous nitrate.

Method of Schoffel.

Take 5 to 10 grams of drillings and dissolve by the well-known method in chloride of copper and ammonium. Collect the residue from the solution and oxidize by nitric acid. Filter, separate the silica by means of hydrofluoric acid, and fuse the residue with sodium carbonate and precipitate with mercurous nitrate. This method is not very exact if the steel contains chromium.

Method of Knorre.

Benzidine, employed frequently for the determination of sulphuric acid, may also be used for the determination of tungsten. Dissolve 20 grams of benzidine in water, dilute to 400 c.c. in a beaker and add 25 c.c. hydrochloric acid, density 1.19. Heat and filter the brown solution and dilute to a liter. One cubic centimeter of this solution is sufficient for 25 milligrams of tungsten, but 20 to 40 per cent. in excess should be used. Begin by adding to the solution to be analyzed a little dilute sulphuric acid or

alkaline sulphate, then add the above solution. The difficultly filterable flakes of benzidine tungstate are precipitated only by crystallized benzidine sulphate. Filter after standing about five minutes. Wash with a dilute solution of benzidine chlor-hydrate, and calcine the wet filter in a platinum crucible. If the precipitation is carried out with the addition of sulphuric acid, it is necessary to take for each centigram of sulphuric acid one c.c. of benzidine solution. With such ores as necessitate the disintegration by sodium carbonate and in which, when evaporated with acid, a little tungsten passes into solution, it is necessary to neutralize with hydrochloric acid and then add a few c.c. of decinormal sulphuric acid before proceeding with the benzidine addition.

With alloys of iron and tungsten, it is necessary to avoid an oxidizing action on the ferric solutions, by dissolving in absence of air in a Jahoda apparatus, using dilute sulphuric acid (density, 1.17) or dilute hydrochloric acid. The tungsten remains in the metallic state in the residue. Wash with a dilute solution of benzidine and fuse the mixture of oxide of iron and tungstic acid with sodium carbonate. Dissolve in water and separate the oxide of iron by filtration, neutralize with hydrochloric acid, acidify with sulphuric acid, and precipitate with benzidine chlor-hydrate.

Method of Von Knobre.

With the view of verifying the applicability of the benzidine chlor-hydrate method for the determination of tungsten in steels, the author has made a series of tests on five samples of steel. He has verified the method just described, the solution of the sample being completed in the absence of air and the avoidance of the oxidation of the pulvurent tungsten, which would give too low results. The solution should in general be made without an excess of acid and the solution should be thoroughly cooled in the absence of air before filtration. Finally, the solution and washing of the tungsten should be made as quietly as possible and through a filter of very fine texture. The observation of these precautions insures good results, while if the solution is carried out in the air, even in the presence of copper sulphate, designed to precipitate metallic copper in the presence of iron to prevent the peroxidation of iron, low results are obtained.

The author recommends the following simplified method: Five to ten grams of sample are dissolved in air in hot dilute hydrochloric acid in an Erlenmeyer flask. Then, when the attack is complete, neutralize until the solution is barely acid with sodium carbonate, that is to say, until the precipitate only redissolves with difficulty. One can also drive off the excess of acid by evaporation to dryness and taking up the residue in a few drops of hydrochloric acid, but this method of procedure takes more time. Add 10 c.c. of decinormal sulphuric acid or alkaline sulphate and 40 to 60 c.c. of benzidine solution. It does not matter if a portion of the tungsten oxidizes to tungsten hydrate, for it is reduced by the addition of benzidine chlor-hydrate to the insoluble benzidine tungstate. To make the precipitation quantitative, it is necessary that very little free acid be present.

After standing for fifteen to twenty minutes to cool, the precipitate containing metallic tungsten and tungstate of benzidine is filtered off and washed with a dilute solution of benzidine, formed by dilution with five to ten times its weight of water. Burn off the paper in a platinum crucible and fuse the residue with carbonate of soda. Dissolve in hot water and filter out the oxide of iron. Add a few drops of methyl orange and neutralize to red coloration with hydrochloric acid. Then add 10 c.c. of deci-normal sulphuric acid and precipitate the tungsten with 40 to 60 c.c. of benzidine chlor-hydrate. Filter, wash and weigh as WO_3. As the benzidine tungstate is soluble in hot water, it is necessary to cool completely before filtration. Contrary to the other methods, the presence of phosphorus is not an inconvenience. The tungstic acid obtained is sufficiently free from silica to render evaporation with hydrofluoric acid unnecessary.

Method of Bazin.

Fuse in a nickel crucible two grams of steel drillings with 4 grams of sodium peroxide and 3 grams of caustic soda.

Allow to cool, dissolve in water, add a few drops of oxygenated water to peroxidize the manganese. Dilute to 250 c.c. and filter off half. Add 20 grams of ammonium nitrate, allow to stand, filter and separate the silica. Precipitate phosphoric acid with magnesium nitrate, and, after allowing to stand for twelve hours,

filter and wash with a solution containing one-third ammonia. Acidulate the filtrate with nitric acid and precipitate with mercurous nitrate.

Method of Lind and Trueblood.

Dissolve 2 to 10 grams of steel in 30 c.c. of nitric acid (1.20), adding, if necessary, 1 to 2 grams of potassium chlorate to insure the complete oxidation of tungsten carbide. Evaporate to dryness and repeat the operation if necessary. Take up in 15 to 20 c.c. of concentrated hydrochloric acid, evaporate almost to dryness, and take up in a little concentrated hydrochloric acid. Dilute to 150 to 200 c.c. and boil strongly for a few minutes. Allow the precipitate to settle, decant on a filter, and wash with dilute hydrochloric acid, 5 to 10 per cent. solution, avoiding pouring the precipitate on the filter until the wash water is free from iron. Complete the washing to get rid of the acid with a 3.5 per cent. solution of mercurous nitrate; this avoids a loss of tungstic acid by passing through the filter as a colloidal solution.

Throw the filter in a Erlenmeyer flask and add excess of N/5 caustic potash solution. The solution of the tungstic acid is facilitated by heating on a steam bath. After cooling titrate with N/5 hydrochloric acid in the presence of phenolphtaleine,

$$1 \text{ c.c. } N/5 \text{ KOH} = 0.0184 \text{ grams W.}$$

The sample analyses given by the authors appear satisfactory; they were made on steels of low silicon content, but they state that high silicon content would not modify them to any appreciable extent.

Method of Kuklin.

The principle of this method is as follows: Meta-tungstic acid is formed by the addition of acids to tungstates in the presence of phosphoric acid and is reduced to the form WO_2 by the action of zinc, which may then be oxidized to tungstic acid by permanganate.

$$5WO_2 + Mn_2O_7 = 5WO_3 + 2MnO.$$

Dissolve 2 grams of steel in a mixture of one part sulphuric acid (density, 1.84) and one part phosphoric acid (density, 1.70) and three parts water. Add permanganate in quantities of 3 c.c.

at a time and heat. To half of the cold solution add 200 c.c. of sulphuric acid (1 : 3) and 40 grams of zinc and heat (if necessary, in a current of carbonic acid). Then treat the mixtures of oxides of iron and tungsten with permanganate. The second half of the solution is treated by Reinhardt's method (by titration with a standard solution of $SnCl_2$) or with stannous chloride and iodine to determine the iron.

The tungsten equivalent of the permanganate may be obtained by multiplying the iron standard by 2.0754.

Ferro-tungsten should be decomposed by fusion with ammonium nitrate and a mixture of carbonates of soda and potassium before attacking with acids. Or, it may be decomposed by fusion with potassium bi-sulphate in a platinum crucible, dissolving in hot water, then with a solution of sodium carbonate, and completing the operation by the above method.

UNIVERSITY OF CALIFORNIA

INDEX.

PAGE.

Absorption of Radio-Active Emanations by Charcoal—R. W. Boyle...429
Acheson, E. G.—Portrait Frontispiece; Address 7; *Discussion*..... 49
Alcohol Solutions at 25 degrees, Solubility of Boric, Camphoric, Benzoic and Salicylic Acids in Aqueous Ethyl—Atherton Seidell...319
Alloying of Calcium and Iron—Alcan Hirsch and James Aston.....143
Alloys for Aluminothermic Work, The Preparation of Calcium—O. P. Watts and J. M. Breckenridge.....153
Aluminothermic Work, The Preparation of Calcium Alloys for—O. P. Watts and J. M. Breckenridge.....153
Aluminum, Industrial Applications of—E. Blough.....165
Aluminum-Magnesium Cell, etc.—H. T. Barnes and G. W. Shearer...169
Aluminum, The Nature of the Surface Film Formed on, etc.—H. T. Barnes and G. W. Shearer.....169
Annealing, The Electrical Testing of Iron During the—E. E. F. Creighton 127
Anodes in Chloride Solutions, Copper—Saul Dushman.....313
Applications of Aluminum, Industrial—E. Blough.....165
Aston, James and Alcan Hirsch—Alloying of Calcium and Iron.....143
Baekeland, L. H.—*Discussion*.....259 *et seq.*, 444
Bancroft, Wilder D.—The Electrochemistry of Light, 243; *Discussion* 50, 98, 241, 261, 285, 307, 337
Barnes, H. T., and G. W. Shearer—The Nature of the Surface Film Formed on Aluminum and the Aluminum-Magnesium Cell.....169
Discussion 172
Bartells, G. C., Jr., and A. T. Lincoln—Additional Experiments on the Electrolytic Corrosion of Brasses.....331
Baskerville, Charles—*Discussion*.....261 *et seq.*
Benzoic Acid, Solubility of, in Aqueous Ethyl Alcohol Solutions at 25 degrees—Atherton Seidell.....319
Betts, Anson G.—*Discussion*.....121 *et seq.*, 263, 307
Bibliography of Electrochemistry and Allied Subjects—P. F. Mottelay.453
Blough, E.—Industrial Applications of Aluminum.....165
Boric Acid, Solubility of in Aqueous Ethyl Alcohol Solutions at 25 degrees—Atherton Seidell.....319
Boyle, R. W.—The Absorption of Radio-Active Emanations by Charcoal 429
Brasses, Experiments on the Electrolytic Corrosion of—A. T. Lincoln and G. C. Bartells, Jr.....331
Breed, George—*Discussion*.....284 *et seq.*, 383 *et seq.*

PAGE

Breckenridge, J. M., and O. P. Watts—The Preparation of Calcium Alloys for Aluminothermic Work.....153
Bronson, Howard L.—The Construction and Accurate Measurement of Resistances of the Order of One Hundred Thousand Megohms.231
Discussion 241
Brown, J. W.—The Use of Dry Cells on Ignition Service, 173; *Discussion* .....182 *et seq.*
Burgess, C. F.—Corrosion of Iron from the Electrochemical Standpoint, 17; *Discussion,* 53 *et seq.,* 96 *et seq.,* 120 *et seq.,* 132, 150, 170 *et seq.,* 181 *et seq.,* 258 *et seq.,* 285 *et seq.*
Calcium and Iron, The Alloying of—Alcan Hirsch and James Aston....143
Calcium Alloys for Aluminothermic Work, The Preparation of—O. P. Watts and J. M. Breckenridge.....153
Camphoric Acid, Solubility in Aqueous Ethyl Alcohol Solutions at 25 degrees—Atherton Seidell.....319
Carhart, H. S.—*Discussion*.....52 *et seq.,* 102, 208 *et seq.,* 344 *et seq.*
Cell, The Aluminum-Magnesium—H. T. Barnes and G. W. Shearer...169
Cell, Temperature Formula of the Weston Standard—F. A. Wolff.....187
Cells on Ignition Service, The Use of Dry—J. W. Brown.....173
Charcoal, the Absorption of Radio-Active Emanations by—R. W. Boyle 429
Chloride Solutions, Copper Anodes in—Saul Dushman.....313
Conductors, On the Nature of Electrolytic—Louis Kahlenberg.....265
Conduit, Electrochemical Corrosion of the Rochester Steel—R. H. Gaines 55
Construction and Accurate Measurement of Resistances of the Order of One Hundred Thousand Megohms—Howard L. Bronson....231
Copper Anodes in Chloride Solutions—Saul Dushman.....313
Corrosion of Brasses, Experiments on the Electrolytic—A. T. Lincoln and G. C. Bartells, Jr.....331
Corrosion of Iron from the Electrochemical Standpoint—C. F. Burgess. 17
Corrosion of Rochester Steel Conduit, Electrolytic—R. H. Gaines.... 55
Creighton, E. E. F.—Electrical Testing of Iron During the Annealing, 127; *Discussion* 131
Currents in Electrolytes without Electrodes, Direct—Carl Hering....273
Directors, Report of Board of..... 9
Distillation of Turpentine by Electricity—F. T. Snyder.....371
Doremus, Charles A.—Robert Hare's Electric Furnace.....347
Dry Cells on Ignition Service, The Use of—J. W. Brown.....173
Durant, Edward—*Discussion*.....424 *et seq.*
Dushman, Saul—Copper Anodes in Chloride Solutions.....313
Electric Furnace, Robert Hare's—Charles A. Doremus.....347
Electric Furnace Conversion of Iron Pyrites into a Magnetic Form—O. L. Kowalke.....133
Electrical Testing of Iron During the Annealing—E. E. F. Creighton..127
Electrochemical Industries, Power for—John Meyer.....377

PAGE
Electrochemical Patents, and Some of the Needs of the United States Patent System—Arba B. Marvin, Jr. 431
Electrochemistry and Allied Subjects, Bibliography of—P. F. Mottelay. 453
Electrochemistry of Light—Wilder D. Bancroft 243
Electrodes, Direct Currents in Electrolytes without—Carl Hering 273
Electrolysis, Reversed—J. W. Turrentine 289
Electrolysis of Nitric Acid Using a Mercury Cathode—J. A. Wilkenson. 309
Electrolytes without Electrodes, Direct Currents in—Carl Hering 273
Electrolytic Conductors, On the Nature of—Louis Kahlenberg 265
Electrolytic Corrosion of Brasses, Experiments on—A. T. Lincoln and G. C. Bartells, Jr. 331
Energy, Kinetic Molecular—Charles P. Steinmetz 397
Ethyl Alcohol Solutions, Solubility of Boric, Camphoric, Benzoic and Salicylic Acids in Aqueous—Atherton Seidell 319
Fleming, R.—*Discussion* 182
Forestry, Water Storage, Power and Navigation—Edward R. Taylor. . 385
Formula of the Weston Standard Cell, Temperature—F. A. Wolff 187
Furnace Conversion of Iron Pyrites into a Magnetic Form, Electric—O. L. Kowalke 133
Furnace, Robert Hare's Electric—Charles A. Doremus 347
Gaines, Richard H.—Electrochemical Corrosion of the Rochester Steel Conduit, 55; *Discussion* ..... 49, 97 *et seq.*
Gin, Gustave—Methods of the Treatment of Simple and Complex Ores of Tungsten 481
Grower, George G.—*Discussion* 51
Hare, Electric Furnace of Robert—Charles A. Doremus 347
Heat of Vaporization of Metals and Other Substances, Latent—Joseph W. Richards 447
Henry, The Early Work of Joseph—James F. McElroy 339
Hering, Carl—Direct Currents in Electrolytes without Electrodes, 273; *Discussion,* 51 *et seq.,* 97 *et seq.,* 171 *et seq.,* 181 *et seq.,* 210, 240 *et seq.,* 284 *et seq.,* 345.
Hibbard, Henry D.—*Discussion* 162
Hirsch, Alcan and James Aston—Alloying of Calcium and Iron, 143; *Discussion* 151
Hutton, R. S., and E. W. Smith—On the Direct Synthesis of Hydrocyanic Acid 359
Hydrocyanic Acid, On the Direct Synthesis of—E. W. Smith and R. S. Hutton 359
Ignition Service, The Use of Dry Cells on—J. W. Brown 173
Iron and Calcium, Alloying of—Alcan Hirsch and James Aston 143
Iron, Corrosion of from the Electrochemical Standpoint—C. F. Burgess 17
Iron, Electrical Testing of During the Annealing—E. E. F. Creighton. 127
Iron, Electrolytic Refining of—E. F. Kern 103
Iron Pyrites, Electric Furnace Conversion of into a Magnetic Form—O. L. Kowalke 133

PAGE
Kahlenberg, Louis—On the Nature of Electrolytic Conductors.....265
Kern, E. F.—Electrolytic Refining of Iron, 103; *Discussion*....122 *et seq.*
Kinetic Molecular Energy—Charles P. Steinmetz.....397
Kowalke, O. L.—Electric Furnace Conversion of Iron Pyrites into a Magnetic Form 133
Latent Heat of Vaporization of Metals and Other Substances—Jos. W. Richards 447
Lidbury, F. A.—*Discussion*.....50, 211, 286 *et seq.*, 306 *et seq.*
Light, The Electrochemistry of—Wilder D. Bancroft.....243
Lincoln, A. T., and G. C. Bartells, Jr.—Additional Experiments on the Electrolytic Corrosion of Brasses, 331; *Discussion*.....337
Magnesium-Aluminum Cell—H. T. Barnes and G. W. Shearer.....169
Marvin, Arba B., Jr.—Electrochemical Patents and Some Needs of the United States Patent System, 431; *Discussion*.....444 *et seq.*
McElroy, James F.—The Early Work of Joseph Henry, 339; *Discussion* 49 *et seq.*, 97 *et seq.*
Measurement of Resistances of the Order of One Hundred Thousand Megohms, The Construction and Accurate—Howard L. Bronson.231
Members Elected and Qualified..... 14
Mercury Cathode, Electrolysis of Nitric Acid Using a—J. A. Wilkinson 309
Meyer, John—Power for Electrochemical Industries.....377
Molecular Energy, Kinetic—Charles P. Steinmetz.....397
Mottelay, P. F.—Bibliography of Electrochemistry and Allied Subjects.453
Navigation, Forestry, Water Storage, Power and—Edward R. Taylor.385
Nitric Acid, Electrolysis of Using a Mercury Cathode—J. A. Wilkinson 309
Patents, and Some Needs of the United States Patent System, Electrochemical—Arba B. Marvin, Jr.....431
Potter, H. N.—*Discussion*.....101, 443
Power for Electrochemical Industries—John Meyer.....377
Power and Navigation, Forestry, Water Storage—Edward R. Taylor..385
Proceedings of the Thirteenth General Meeting..... 1
Pyrites into a Magnetic Form, Electric Furnace Conversion of Iron—O. L. Kowalke.....133
Radio-Active Emanations, The Absorption of by Charcoal—R. W. Boyle 429
Refining of Iron, Electrolytic, Edward F. Kern.....103
Raegener, Louis C.—*Discussion*.....442 *et seq.*
Report of Board of Directors..... 9
Report of Secretary..... 10
Report of Tellers..... 3
Report of Treasurer..... 13
Resistances of the Order of One Hundred Thousand Megohms, The Construction and Accurate Measurement of—Howard L. Bronson 231

PAGE
Reversed Electrolysis—J. W. Turrentine.....289
Richards, Jos. W.—Latent Heat of Vaporization of Metals and Other Substances, 447; *Discussion,* 120, 131 *et seq.,* 150 *et seq.,* 162 *et seq.,* 183, 285 *et seq.,* 337, 426 *et seq.*
Rochester Steel Conduit, Electrochemical Corrosion of—R. H. Gaines. 55
Salicylic Acid, Solubility of in Aqueous Solutions of Ethyl Alcohol at 25 degrees—Atherton Seidell.....319
Secretary, Report of..... 10
Seidell, Atherton—Solubilities of Boric, Camphoric, Benzoic and Salicylic Acids in Aqueous Ethyl Alcohol Solutions at 25 degrees..319
Sharp, Clayton H.—*Discussion* .....51, 98 *et seq.*
Shearer, G. W., and H. T. Barnes—The Nature of the Surface Film Formed on Alumnium and the Aluminum-Magnesium Cell.....169
Smith, A. W.—*Discussion*.....121, 131, 163
Smith, E. W., and R. S. Hutton—On the Direct Synthesis of Hydrocyanic Acid.....359
Snyder, F. T.—Distillation of Turpentine by Electricity.....371
Solubilities of Boric, Camphoric, Benzoic and Salicylic Acids in Aqueous Ethyl Alcohol Solutions at 25 degrees—Atherton Seidell 319
Steinmetz, Charles P.—Kinetic Molecular Energy, 397; *Discussion,* 132, 427, 443 *et seq.*
Tellers, Report of..... 3
Temperature Formula for the Weston Standard Cell—F. A. Wolff....187
Taylor, Edward R.—Forestry,. Water Storage, Power and Navigation.385
Testing of Iron During the Annealing, Electrical—E. E. F. Creighton..127
Treasurer, Report of..... 13
Tungsten, Methods of Treatment of Simple and Complex Ores of—Gustave Gin.....481
Turpentine, Distillation of by Electricity—F. T. Snyder.....371
Turrentine, J. W.—Reversed Electrolysis.....289
Units for International Adoption, Principles Involved in the Selection and Definition of the Fundamental—F. A. Wolff.....213
Vaporization of Metals and Other Substances, Latent Heat of—Jos. W. Richards 447
Water Storage, Power and Navigation, Forestry—Edward R. Taylor..385
Watts, O. P., and J. M. Breckenridge—The Preparation of Calcium Alloys for Aluminothermic Work, 153; *Discussion*.....163
Weston Standard Cell, Temperature Formula of the—F. A. Wolff....187
Whitney, W. R.—*Discussion*.....170 *et seq.*
Wilkinson, J. A.—Electrolysis of Nitric Acid Using a Mercury Cathode 309
Wolff, F. A.—Principles Involved in the Selection and Definition of the Fundamental Units for International Adoption.....213
Temperature Formula for the Weston Standard Cell.....187
Discussion.....50, 209 *et seq.,* 239 *et seq.*

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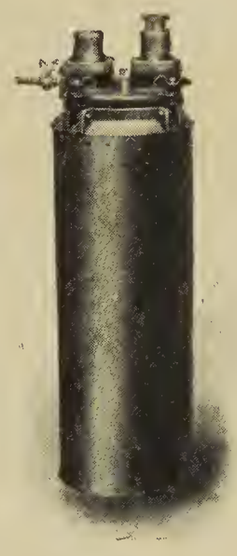

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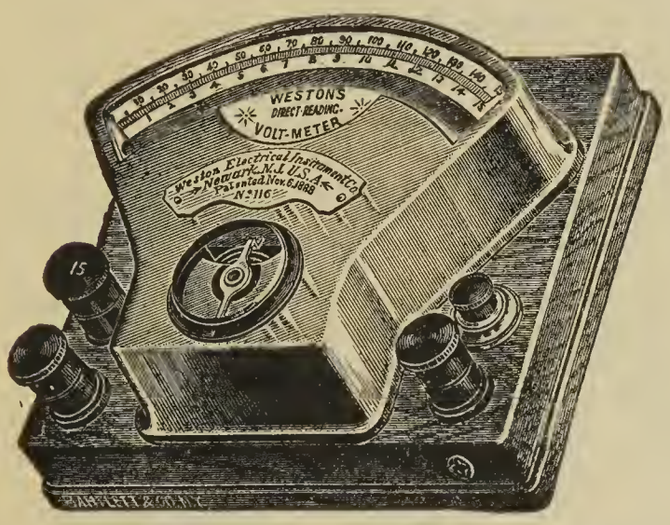

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